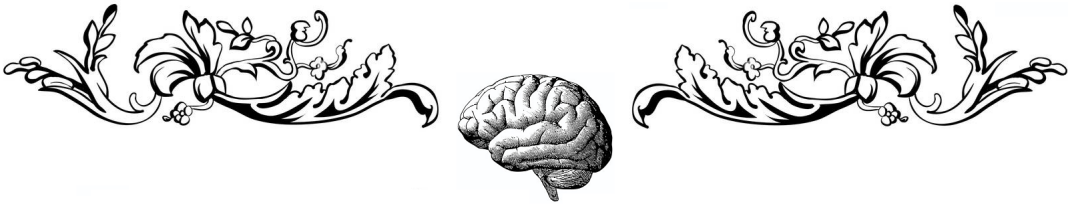

Article

The Theory of Electrolytes I. and II.

Author:
Peter Joseph William Debye
March 24, 1884, Maastricht –
November 2, 1966, New York

Author:
Erich Armand Arthur Joseph
Hückel
August 9, 1896, Berlin –
February 16, 1980, Marburg

Physikalische Zeitschrift, Vol. 24, (1923), pp 185–206 and 305–325

Contents

List of Symbols 3

I. The Theory of Electrolytes. I. Freezing Point Depression and Related Phenomena 7

1. Introduction 8

2. Fundamentals 12

3. Calculation of the Electrical Energy of an Ionic Solution of an Uni-univalent Salt 17
3.1. Vanishing Ion Diameter 20
3.2. Finite Ion Diameter 22

4. The Potential Energy of an Arbitrary Ionic Solution 24

5. The Additional Electric Term to the Thermodynamic Potential 27

6. Osmotic Pressure, Vapor Pressure Depression, Freezing-Point Depression, Boiling-Point Elevation 30

7. The Freezing-Point Depression of Dilute Solutions 35

8. The Dissociation Equilibrium 40

9. Comparison of Freezing-Point Depression with Experimental Empirical Data 43

10. General Remarks 56

II. The theory of electrolytes. II. The Limiting Law for Electrical Conductivity 60

1. Introduction 61

2. Ionic Forces **65**
2.1. Fundamental Equation to Determine the Distribution Function . . . 65
2.2. Generell Conditions to Determine the Ionic Cloud 67
2.3. Approximations and Their Physical Meaning 69
2.4. The Potential Distribution Around a Moving Ion 71
2.5. Field and Charge Distribution Around a Moving Ion 74

3. Electrophoretic Forces **78**
3.1. Equations of Motion for the Solvent 78
3.2. General Form of the Distribution of Velocity and Pressure 80
3.3. Fulfillment of Boundary Conditions. Total Transmitted Force 85

4. Conductivity **89**
4.1. The Coefficient of Conductivity 89
4.2. Discussion of the Coefficient of Conductivity 92

5. Comparison with Empirics **97**
5.1. Aqueous Solutions of uni-univalent Salts 97
5.2. Aqueous Solutions of Salts with Polyvalent Ions 104
5.2.1. Mono- and Divalent Salts 104
5.2.2. Di-Divalent Salts 107
5.3. Non-Aqueous Solvents 107
5.4. Temperature Dependence of the Coefficient of Conductivity 112

III. Appendix **114**

IV. Literature **117**

References **123**

List of Symbols

a, a_i	ion size, size of the i-th ion, m
b	radius of moving sphere, m
c_i	Molar concentration or substance concentration of the i-th type of ion in the solution, $= \frac{n}{V}$, $\mathrm{mol\,m^{-3}}$ or $\mathrm{mol\,L^{-1}}$
c_p	specific heat of the liquid solvent at constant pressure, $\mathrm{J\,kg^{-1}\,K^{-1}}$
c'_p	specific heat of the frozen solvent at constant pressure, $\mathrm{J\,kg^{-1}\,K^{-1}}$
e_0	elementary charge, $1.602\,176\,634 \times 10^{-19}\,\mathrm{C}$; $1\,\mathrm{C} = 1\,\mathrm{A\,s} = 2\,997\,924\,580\,\mathrm{statC}$
$e^{-\frac{q\Psi}{k_\mathrm{B}T}}$	Boltzmann factor
$\mathscr{E}$	electric field strength, $\mathrm{V\,m^{-1}}$ or $\mathrm{N\,C^{-1}}$
$\mathscr{E}_x, X$	x component of the electric field strength, $\mathrm{V\,m^{-1}}$ or $\mathrm{N\,C^{-1}}$
$\mathfrak{F}$	Force regarding volume, Force, N
f_a	activity coefficient, dimensionless
f_0	osmotic coefficient, dimensionless
f_λ	coefficient of conductance, dimensionless
G	Gibbs free energy, J
$H_{\mathrm{m,fus}}$	molar enthalpy of fusion, $\mathrm{J\,mol^{-1}}$
H_{fus}	heat of fusion of the frozen solvent, J
$\mathfrak{K}$	Force, Force acting on a particle, N
K	equilibrium constant
k_B	Boltzmann constant, $1.380\,649 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
$\overline{L}, \overline{L}_i$	Mobility (of the i-th ion)
n	amount of substance, mol
n_i	distribution/number concentration of ion i per volume or in an electrolyte, $\mathrm{m^{-3}}$

$\overline{n_i}$	mean value of the distribution/number of ions per volume, m^{-3}
N_A	AVOGADRO constant, $6.022\,140\,76 \times 10^{23}\,\mathrm{mol}^{-1}$
N, N_i	number of individual molecules, particles or ions (in the solution), $N = n \cdot N_A$, mol^{-1}
p	external pressure, Pa
p_e	electric pressure, Pa
P	actual osmotic pressure, Pa
P_k	osmotic pressure, Pa
$q, -q/+q, q_1, q_2$	electric charge in COULOMB, point charge, equals $z \cdot e_0$, $1\,\mathrm{C} = 1\,\mathrm{A\,s}$
Q	melting heat of one mole, $\mathrm{J\,mol}^{-1}$
r	distance, distance from the highlighted ion m
$\mathscr{R}$	molar gas constant $8.314\,462\,618\,153\,24\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1}$
S	entropy, $\mathrm{J\,K}^{-1}$
$\mathrm{d}S$	volume element, space element
T	temperature, K
T_0	freezing point of the pure solvent, K
U	energy, J
U_e	electrical energy, W s
V	volume, m^3 or L
$\mathbf{v}, \mathfrak{v}$	(fluid) velocity, velocity of ion, $\mathrm{m\,s}^{-1}$
$\mathfrak{w}$	vorticity, s^{-1}, $\mathfrak{w} = \nabla \times \mathbf{v} = \left(\frac{\partial v_z}{\partial y} - \frac{\partial v_y}{\partial z}, \frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x}, \frac{\partial v_y}{\partial x} - \frac{\partial v_x}{\partial y}\right)$
w_1, w_2	valence factor, according to Equation 4.9”
w	distribution function group
x, y, z	Cartesian components of the coordinate system moving with the ion and relative to X, Y, Z group
X, Y, Z	Cartesian components of the (rigid) inertial System group
z_i	charge number or charge on species i, $1, 2, \ldots, i, \ldots, s$, in signed units of electronic charge respectively, dimensionless, refers to a quantized value of electric charge of an ion

γ	concentration, measured concentration, $\mathrm{mol\,L^{-1}}$
Δ	temperature, K, see page 33, Freezing point depression
Δ_k	Freezing point depression to be expected at complete dissociation, K
Δ	= div grad, LAPLACE-operator, representation in three dimensions (x, y, z): $\Delta f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}$; in spherical coordinates (r, ϑ, φ): $\Delta f = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\,\frac{\partial f}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\,\frac{\partial f}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 f}{\partial \varphi^2}$
ε	permittivity, $\mathrm{A\,s\,V^{-1}\,m^{-1}}$; the absolute permittivity, often simply called permittivity is a measure of the electric polarizability of a dielectric material. It is expressed as the product of the relative permittivity (in German formerly known as "Dielektrizitätskonstante") with the electric permittivity of a vacuum, $\varepsilon = \varepsilon_r \cdot \varepsilon_0$
ε_r	relative permittivity; the relative permittivity (in older texts, dielectric constant) is the permittivity of a material expressed as a ratio with the electric permittivity of a vacuum. It is dimensionless.
ε_0	vacuum permittivity, $8.854\,187\,818\,8 \times 10^{-12}\,\mathrm{F\,m^{-1}}$ or $8.854\,187\,818\,8 \times 10^{-12}\,\mathrm{A\,s\,V^{-1}\,m}$, an old German designation is "Influenzkonstante"
$\mathrm{d}\zeta$	surface element of a sphere
η	dynamic viscosity, Pa s
Θ	$\frac{\Delta_k - \Delta}{\Delta_k} = 1 - f_0$, dimensionless
$\varkappa^{-1}$	reciprocal characteristic length, DEBYE screening length, $\mathrm{m^{-1}}$
λ	electrolytic conductivity, specific conductance of an electrolyte, $\mathrm{S\,m^{-1}}$ or $\Omega^{-1}\,\mathrm{m^{-1}}$
λ_0	limiting electrolytic conductivity, limiting specific conductance of an electrolyte, $\mathrm{S\,m^{-1}}$ or $\Omega^{-1}\,\mathrm{m^{-1}}$
$\Lambda_\mathrm{m}, \overline{\Lambda}_\mathrm{m}$	molar conductivity, electrostatic units or $\mathrm{S\,m^2\,mol^{-1}}$
$\Lambda^0_\mathrm{m}, \overline{\Lambda}^0_\mathrm{m}$	limiting molar conductivity, electrostatic units or $\mathrm{S\,m^2\,mol^{-1}}$

μ	deviation from the equilibrium distribution or the MAXWELL-BOLTZMANN distribution, respectively, m^{-3}
ν_i	number, to which the i ions decompose (disintegration number)
ξ_i, ξ	(components $i = 1, 2, 3, \ldots$ of the) coefficient of friction (dimensionless scalar value)
$\varrho(r)$	(electric) charge density, $\mathrm{C\,m}^{-3}$
σ_i	function of $x_i = \varkappa \cdot a_i$, see Equation 6.5
τ	very small interval of time, s
φ_i	thermodynamic potential related to one particle i, $\mathrm{J\,K}^{-1}$
ϕ	quotient of the coefficients of friction according to Equation 4.13
$\Phi(P, T)$	thermodynamic potential, J
ψ	electrostatic potential, value of the scalar electric potential field at a point P, see page 17, $\mathrm{V} = \mathrm{kg\,m^2\,s^{-3}\,A^{-1}}$
ω	abbreviation for $\frac{\xi \mathbf{v}}{k_\mathrm{B} T}$

$_i$	i-th type or kind of particle or ion, $i = 1, 2, 3, \ldots$
$_n$	index of summation, $n = 1, 2, 3, \ldots$
$_0$	related to the solvent
$_s$	species of ion, e.g. a molecule dissociates in s species of ions, where the different types are numbered according to $1, \ldots, i, \ldots s$

Part I.

The Theory of Electrolytes. I. Freezing Point Depression and Related Phenomena

1. Introduction

As we know ARRHENIUS' hypothesis of dissociation explains the abnormally large values of osmotic pressure, freezing point depression, etc., observed in electrolyte solutions, because the existence of ions goes hand in hand with an increase in the number of individual particles. The quantitative theory is based on the extension of the laws of ideal gases, which VAN'T HOFF introduced, to dilute solutions for the calculation of their osmotic pressure. Because it is possible to justify this extension via thermodynamics, there is no doubt as to the general validity of these fundamentals.

At finite concentrations, however, values for freezing point depression, conductivity, etc. are smaller than would be expected at first consideration in the presence of *complete* dissociation of the electrolytes into ions. If we let, for instance, P_k be osmotic pressure, which results from VAN'T HOFF's classical law for perfect dissociation, then the actual osmotic pressure observed is smaller, such that

$$P = f_0 \cdot P_k \,,$$

in agreement with BJERRUM, [7, 9], where the "osmotic coefficient" f_0 thus introduced which is independent of any theory, is intended to measure those deviations and is observable as a function of concentration, pressure, and temperature. In reality, such observations are not directly related to the osmotic pressure itself but to freezing point depression or boiling point elevation, both deducible for thermodynamic reasons using the same osmotic coefficient f_0 from their limiting values according to VAN'T HOFF's law of complete dissociation.

The most obvious assumption to explain the presence of this osmotic coefficient is the classical one, according to which not all molecules are dissociated into ions, but an equilibrium exists between dissociated and undissociated molecules that depends on the total concentration, as well as on pressure and temperature. The number of free individual particles is therefore variable, and indeed it would have to be set directly proportional to f_0. The quantitative theory of these dependencies, as far as it relates to the concentration, relies on GULDBERG-WAAGE's law of mass action; the dependence on temperature and pressure of the equilibrium constant appearing in this law is to be determined thermodynamically according to VAN'T HOFF. The whole group of all dependencies, including GULDBERG-WAAGE's approach, can be based on thermodynamics, as PLANCK showed.

Because the electrical conductivity is determined solely by the ions and, according to the classical theory, the number of ions immediately follows from f_0, this theory requires the well-known relationship between the two dependencies on conductivity the one hand and osmotic pressure on the other from concentration.

A large group of electrolytes, the strong acids, bases, and their salts, grouped under the name of "strong" electrolytes, shows pronounced deviations demanded by the classical theory, which, remarkably, are all the clearer the more dilute the solutions are[1]. Therefore, as it was realized in the course of its development, that it was only possible with an approximation to deduce from f_0, demanded by the classical theory, the dependence of conductivity from concentration. Furthermore, the dependence of the osmotic coefficient f_0 itself on the concentration is quite incorrectly represented. For heavily diluted solutions, f_0 approaches 1; if we now plot $1 - f_0$ as a function of the concentration c, the classical theory for binary electrolytes, such as KCl, requires that this curve intersects with the origin (*Nullpunkt*) with a finite tangent (determined by the equilibrium constant K). If the molecule of the electrolyte generally dissociates into ν ions, then, according to the law of mass action, for small concentrations there results:

$$1 - f_0 = \frac{\nu - 1}{\nu} \cdot \frac{c^{\nu-1}}{K} ,$$

such that in cases where the dissociation occurs in more than two ions, the curve in question must have a contact of an even higher order with the abscissa. The complex of these dependencies is represented by Wilhelm Ostwald's law of dilution.

Actually, observations of strong electrolytes show quite a different behavior[2]. The experimental curve exits the origin at a right angle (see Figure 9.1) to the abscissa, independent of the number of ions, ν. All proposed practical interpolation formulæ attempt to model this behavior by setting $1 - f_0$ to be proportional to a fractional power (less than 1, about $1/2$ or $1/3$) of the concentration. The same phenomenon repeats itself in case of extrapolation of the conductivity to infiniteimal dilution,

[1] A summary of this subject was reported by L. Ebert, [13]

[2] Strong electrolytes are those, which are completely dissociated irrespective of their concentration. They should show a linear dependence of the conductivity on concentration. However, this relationship is only approximately true even for dilute solutions. At higher concentrations, the conductivity rises less rapidly than expected from extrapolation of the results in dilute solutions, owing to the increasing inter-ionic interactions as the mean distance between ions decreases. Given that electrostatic forces increase with the inverse square of the separation between ions, and that sucg forces between oppositely charged ions would be expected to hinder the mobility, this behavior at higher concentrations can be rationalized, [23].

which according to KOHLRAUSCH is to be done using a power of 1/2.

It is clear that, under these circumstances, the classical theory cannot be maintained. On the contrary, all experimental material clearly indicates that it can also be abandoned in its fundamental concept, and, in particular, that a calculated equilibrium according to GULDBERG-WAAGE's approach does not correspond the real phenomena.

W. SUTHERLAND, [59], in 1907 even attempted to establish the theory of electrolytes on the assumption of complete dissociation. His work contains some good thoughts. N. BJERRUM, [6], is probably the one who first came to a correctly delineated formulation of that hypothesis. He has clearly stated and argued that in the case of the strong electrolytes, there is no apparent equilibrium between dissociated and undissociated molecules and that there are compelling reasons for considering such electrolytes to be dissociated into ions in their entirety up to high concentrations. Only when considering weak electrolytes do undissociated molecules occur again. Therefore the classical explanation falls short as the sole basis for the variability of, for instance, the osmotic coefficient, and the task arises to search for a hitherto overlooked effect of the ions, which, despite the absence of an association, could explain the decrease of f_0 with increasing concentration.

More recently, under the influence of BJERRUM, it has been suggested that the consideration of the electrostatic forces that the ions exert on each other, and which, because the relatively high value of the electric elementary charge should be strongly important, shall provide the desired explanation. Such forces are not mentioned in the classical theory, which rather treats the ions as completely independent entities. The theory as it is conceived corresponds approximately to the transition from the laws describing perfect gases to the theory describing real gases according to VAN DER WAALS. However, we must resort to completely different tools, because the electrostatic forces between the ions decrease only with the square of the distance and thus differ substantially from the molecular forces, which decrease much more rapidly with increasing distance.

For the osmotic coefficient there exists a calculation by MILNER, [49, 51]. It is flawless in its structure but has mathematical difficulties that are not completely overcome and obtaines its result only in the form of a graphically determined curve for the relation between $1-f_0$ and the concentration. Moreover, it will be seen from the following that the comparison with experience that MILNER sets out supports the admissibility of his neglections at excessively high concentrations, for which the individual properties of the ions, which MILNER does not take into account, already play a very important role. Still, it would be unjustified to discount MILNER's

calculations in favor of the recent accounts of J. Ch. Ghosh, [16, 17, 18, 19, 20], on the same topic. In what follows, we shall do a recursion why we cannot agree with Ghosh's calculations in their application to conductivity nor their somewhat more transparent application to the osmotic pressure. We are even forced to call his calculation of the electrostatic energy of an ionized electrolyte, which is the basis for all his further conclusions, fundamentally wrong.

Quite similar to the calculations of the osmotic coefficient are the conditions for the calculation of conductivity. Again, the theory must capture the mutual electrostatic influence of the ions with respect to their mobility. An attempt in this direction comes from P. Hertz, [26]. He transfers the methods of kinetic gas theory and actually finds a mutual interference between the ions. Meanwhile, the transfer of those methods, and in particular the use of terms that correspond to the free path of dilute gases, seems to be highly in question in the case of free ions between the molecules of the solvent. Indeed, the final result by Hertz for small concentrations is irreconcilable with the experimental results.

In this first part, we will deal exclusively with the "osmotic coefficient" f_0 and a similar one used by Bjerrum, [8], in its significance emphasised "activity coefficient" f_a. Even in the case of such (weak) electrolytes, where a significant number of undissociated molecules is present, it cannot simply be determined according to Guldberg-Waage's approach in its classical form

$$c_1^{\mu_1} \cdot c_2^{\mu_2} \cdot \ldots \cdot c_n^{\mu_n} = K\,,$$

where $c_1, c_2, \ldots, c_n$ are the concentrations and K is the equilibrium constant respectively. Rather, one has to write, with respect to the electrostatic forces of the ions, instead of K,

$$f_a \cdot K\,,$$

introducing an activity coefficient[3] f_a. This coefficient, like f_0, will depend on the concentration of ions. Although according to Bjerrum there exists a thermodynamically based relationship between f_a and f_0, the relationship of the two coefficients regarding concentration is different.

The detailed discussion of conductivity we will reserve for a future part, Part II, a classification, which is structurally justified. Whereas the determination of f_0 and f_a can be done by using only reversible processes, the calculation of mobilities requires essentially irreversible processes in which there is no longer a direct link to classical thermodynamic laws.

[3]The activity coefficient f_a introduced here is not completely identical to that introduced by Bjerrum. Namely, Bjerrum splits our coefficient f_a into a product of coefficients, each of which is unique to the individual ionic species. (See chapter 8)

2. Fundamentals

It is known that in thermodynamics it is shown that the properties of a system are completely known if one of the many possible thermodynamic potentials is given as a function of the properly chosen variables. Corresponding to the form of how the terms based on the mutual electrical effects will appear, we may consider the quantity[1]

$$G = S - \frac{U}{T} \tag{2.1}$$

to be the basic function. As variables here (in addition to the concentration) we have obviously volume and temperature, of course, because

$$\mathrm{d}G = \frac{p}{T} \cdot \mathrm{d}V + \frac{U}{T^2} \cdot \mathrm{d}T\,. \tag{2.1'}$$

The calculations to be carried out below differ from the classical ones in that the electrical effects of the ions are taken into account. Accordingly, we decompose U into two components, a classical component U_k and an additional electrical energy U_e:

$$U = U_k + U_e\,.$$

If we consider that, according to Equation 2.1,

$$T^2 \cdot \frac{\partial G}{\partial T} = U\,, \tag{2.2}$$

and also divide the potential G into two parts:

$$G = G_k + G_e\,,$$

we find that, according to Equation 2.2

$$G_e = \int \frac{U_e}{T^2}\,\mathrm{d}T\,. \tag{2.3}$$

Our main task is therefore to determine the electrical energy U_e of an ionic solution. For practical reasons, however, the potential G is not as suitable as Planck's

[1]The potential G differs from the Helmholtz free energy $F = U - TS$ only by the factor $-\frac{1}{T}$. By itself, this difference is negligible; we define, as it appears in the text, a direct connection to Planck's thermodynamics.

preferred function

$$\Phi = S - \frac{U + pV}{T} \,. \tag{2.4}$$

As the differential form of the definition

$$\mathrm{d}\Phi = -\frac{V}{T} \cdot \mathrm{d}p + \frac{U + pV}{T^2} \cdot \mathrm{d}T \tag{2.4'}$$

shows, the variables inherent to the potential Φ are pressure and temperature, and, because the vast majority of experiments are performed at constant pressure (and not at constant volume), Φ is to be preferred. A comparison of Equation 2.4 with Equation 2.1 yields

$$\Phi = G - \frac{pV}{T} \,; \tag{2.5}$$

so if G according to the above is known, then we must find and add the term $-\frac{pV}{T}$ as a function of p and T. Considering equation (1'), we can conclude that

$$\frac{p}{T} = \frac{\partial G}{\partial V} = \frac{\partial G_k}{\partial V} + \frac{\partial G_e}{\partial V} \,, \tag{2.6}$$

and so have obtained the equation of state that relates pressure, volume, and temperature with each other for the ionic solution. It can be interpreted by stating that, as a consequence of the electrical effect of the ions, added to the external pressure p is an additional electric pressure p_e, which is to be calculated from the relation

$$p_e = \frac{\partial G_e}{\partial V} \,. \tag{2.6'}$$

We will later have the opportunity (cf. the note in [2]) to determine this electrical pressure p_e; For an aqueous solution of KCl, for example, at a concentration of 1 mole per liter, it is only about 20 atm. Strictly speaking, it is not correct to use the classical approach for V (as a function of p and T) without considering the electrical effects of the ions, because the pressure p_e also causes a change in volume. However, as the compressibility of water has such a low value that 20 atmospheres cause only a relative volume change of 0.001, the additional electrical effect to V (as a function of p and T) can be neglected. Furthering this observation, we will also decompose Φ into a classical part and an additional electric component

$$\Phi = \Phi_k + \Phi_e \tag{2.7}$$

and, following Equation 2.3, we can set

$$\Phi_e = G_e = \int \frac{U_e}{T^2} \, \mathrm{d}T \,. \tag{2.7'}$$

The classical component Φ_k has, according to PLANCK, the form:

$$\Phi_k = \sum_0^s N_i \cdot (\varphi_i - k_\mathrm{B} \log(c_i)) \ , \tag{2.7"}$$

where

$$N_0, N_1, N_2, \ldots, N_i, \ldots, N_s$$

signify the numbers of individual particles in the solution, and N_0 shall refer specifically to the solvent[2]. Furthermore the thermodynamic potential referring to one single particle:

$$\varphi_i = s_i - \frac{u_i + p \cdot v_i}{T}$$

is a quantity independent of the concentration; k_B is the BOLTZMANN constant, $k_\mathrm{B} = 1.346 \times 10^{-16}\,\mathrm{erg\,Grad^{-1}}$ and c_i signifies the concentration of particle i, such that

$$c_i = \frac{N_i}{N_0 + N_1 + N_2 + \cdots + N_i + \cdots + N_s} \ ,$$

from which the relation

$$\sum_0^s c_i = 1$$

follows.

Having completed these preliminary remarks on thermodynamics, we come to the discussion of the main task: calculation of the electrical energy U_e.

At first glance, it seems as if this energy would be obtained directly in the following way. If, in the solvent with the dielectric constant ε, there are two electric charges of magnitudes q_1 and q_2 (or $+q$ and $-q$) at a distance r, then their mutual

[2]Our relation differs from PLANCK's in that we do not count the number of moles but the actual number of particles, which proves to be more suited to our purposes. This corresponds to the occurrence of the BOLTZMANN constants k_B instead of the gas constant $\mathscr{R}$. An essential difference from PLANCK is, of course, not caused by the above formulation.

potential energy is[3]

$$-\frac{1}{\varepsilon}\cdot\frac{q^2}{r}\,.$$

For simplicity, in this general derivation we consider a binary electrolyte such as KCl that has completely dissociated into ions such that there exist, in the volume V of the solution, $N_1 = N$ K-ions with the charge $+q$ or q_1 and an equal number $N_2 = N$ Cl-ions with the charge $-q$ or q_2. It can then be imagined that the mean distance r, which plays a role in the calculation of the energy, equals the mean distance between the ions, and because the volume associated with one ion is equal to $\frac{V}{2\cdot N}$, we write

$$r = \sqrt[3]{\frac{V}{2\cdot N}}$$

By using this value for r, one would estimate the electrical energy of the solution to be

$$U_e = -N\cdot\frac{q^2}{\varepsilon}\cdot\sqrt[3]{\frac{2\cdot N}{V}}\,.$$

In fact, J. Ch. Ghosh, [16, 17, 18, 19, 20], proceeds in this way. This approach, however, is fundamentally wrong, and the entire theory built upon it (practically characterized by the introduction of the cube root of concentration) must be rejected.

The (negative) electrical energy of an ionic solution results from the fact that, when one looks at any one ion, there are more often found dissimilar ions of the same form in its surrounding than ions with the same kind of charge, an immediate consequence of the electrostatic forces acting between the ions. An exemplary case are crystals such as NaCl, KCl, etc., in which, according to Bragg's investigations, each atom (which also occurs here as an ion) is instantly surrounded by dissimilar ones. As true as it may seem in this case (in accordance with the precise calculations of M. Born) to estimate the electrical energy of the crystal based on the distance of two neighboring dissimilar atoms, the more it is a mistake to overstate the analogy by using the mean distance $\sqrt[3]{\frac{V}{2\cdot N}}$ for calculating a solution. In fact, a totally different length plays a role for the energy, because the ions are free to move and therefore the length only appears later due to the evaluation of

[3]The following example should help clarify the calculation using units.
The absolute permittivity ε is equal to $(\varepsilon_r\cdot\varepsilon_0)$. ε_r is dimensionless and ε_0 has the unit $\mathrm{A\,s\,V^{-1}\,m^{-1}}$. The charge q has the unit Coulomb which equals A s and 1 V equals $1\,\mathrm{kg\,m^2\,A^{-1}\,s^{-3}}$. r has the dimension meter, m. So finally we have:

$$\frac{1}{\frac{\mathrm{A\,s}}{\mathrm{V\,m}}}\cdot\frac{(\mathrm{A\,s})^2}{\mathrm{m}} = \mathrm{A\,s\,V} = \mathrm{A\,s}\cdot\frac{\mathrm{kg\,m^2}}{\mathrm{A\,s^3}}$$

which, after canceling out the duplicate factors, yields the unit Joule, which is $\mathrm{kg\,m^2\,s^{-2}}$.

differences in the probability of residence times of similar and dissimilar ions in the same volume element[4] near a highlighted ion. Even from this it follows that the thermally induced movement should play an essential role in the calculation of U_e.

In terms of dimensions, one can only conclude not more than: assuming the size of the ions need not be taken into account for very dilute solutions[5], one kind of energy is the expression already given above

$$\frac{q^2}{\varepsilon} \cdot \sqrt[3]{\frac{2 \cdot N}{V}} \,.$$

However, another kind of energy of thermally induced movement, measured by $k_\mathrm{B}T$, plays an equal role. It is therefore to be expected that U_e will take the form

$$U_e = -N \cdot \frac{q^2}{\varepsilon} \cdot \sqrt[3]{\frac{2 \cdot N}{V}} \cdot f\left(\frac{\frac{q^2}{\varepsilon} \cdot \sqrt[3]{\frac{2 \cdot N}{V}}}{k_\mathrm{B}T}\right) , \tag{2.8}$$

where f is a function of the ratio of the two energies about which we cannot make any statement *a priori*[6].

The investigation of the limiting case of high temperatures also leads to the same conclusion. If the energy of the thermally induced movement is large, and if one considers a volume element in the vicinity of a highlighted ion for this consideration, then the probability that an ion of the same kind is found there is the same as the probability for a dissimilar one. So in the high temperature limit, U_e must vanish, i.e. the expression for U_e contains T as an essential parameter also at medium temperatures.

[4]For a definition of a volume element in Euclidean space see `https://en.wikipedia.org/wiki/Volume_element`

[5]It will be shown below that this assumption is indeed true.

[6]The considerations of O. Klein agree with this discussion of dimensions: Meddelanden från K. Vetenskapsakademiens Nobelinstitut **5**, Nr. 6, 1919 (A commemoration of the 60th birthday of S. Arrhenius).

3. Calculation of the Electrical Energy of an Ionic Solution of an Uni-univalent Salt

In a volume V, N molecules of a uni-univalent salt (for example, KCl) are dissociated into ions; Let the absolute value of the charge of an ion be e_0 (4.77×10^{-10} e.s.u.), and let the dielectric constant be ε. We consider one of these ions with the charge $+e_0$[1] and intend to determine its potential energy u relative to the surrounding ions. The direct calculation, as attempted by MILNER, taking into account every possible arrangement of the ions and using further for their probability BOLTZMANN's principle, has proved to be mathematically too difficult. We therefore replace the probability with another consideration, in which the calculation is aimed in advance towards the mean value of the electric potential generated by the ions.

At a point P in the vicinity of the highlighted ion, let the mean electric potential be ψ with respect to time; if one brings a positive charged ion to that location, then the work required is $+e_0 \cdot \psi$, while for a negative ion the work $-e_0 \cdot \psi$ is required. In a volume element $\mathrm{d}V$ at this point with respect to time, therefore, we will find a mean value, according to the BOLTZMANN principle, of

$$n \cdot e^{-\frac{e_0 \psi}{k_\mathrm{B} T}} \, \mathrm{d}V$$

positive and

$$n \cdot e^{+\frac{e_0 \psi}{k_\mathrm{B} T}} \, \mathrm{d}V$$

negative ions, if one sets $n = \frac{N}{V}$. In fact, in the limit for $T = \infty$, the distribution of the ions must become uniform, such that the factor in front of the exponential function is equal to $\frac{N}{V}$, i.e. must be set equal to the number of ions of one kind per

[1] In general, because the charge of free particles (e.g. an ion) is always an integer multiple of the elementary charge e_0, the following holds:

$$\pm q = e_0 \cdot \pm z \,,$$

where z is the valency of the appropriate ion. If we therefore consider an univalent ion with valency $+1$, we have $q = e_0 \cdot 1 = e_0$, which shows that our considered ion has a charge corresponding to the absolute value $e_0 = 4.77 \times 10^{-10}$ e.s.u. or 1.6022×10^{-19} C.

cm^3 of the solution. So far, however, no statements can be made with these data, because the potential ψ of the point P is still unknown. According to POISSON's equation, however, the potential must satisfy the condition

$$\Delta\psi = -\frac{4\pi}{\varepsilon} \cdot \varrho \,,$$

if the electricity is distributed with the density ϱ in the medium with a dielectric constant ε. On the other hand, after what was said above, it follows

$$\varrho = ne_0 \cdot \left(e^{-\frac{e_0\psi}{k_\mathrm{B}T}} - e^{+\frac{e_0\psi}{k_\mathrm{B}T}} \right) = -2ne_0 \cdot \sinh\left(\frac{e_0\psi}{k_\mathrm{B}T}\right) ; \tag{3.1}$$

so ψ can be determined as the equation's solution:

$$\Delta\psi = \frac{8\pi ne_0}{\varepsilon} \cdot \sinh\left(\frac{e_0\psi}{k_\mathrm{B}T}\right) . \tag{3.2}$$

The further one moves away from the highlighted ion, the smaller will be the potential ψ, and for larger distances the sufficient approximation $\sinh\left(\frac{e_0\psi}{k_\mathrm{B}T}\right)$ can be replaced by $\frac{e_0\psi}{k_\mathrm{B}T}$. If one applies this substitution, Equation 3.2 takes on the much simpler form[2]

$$\Delta\psi = \frac{8\pi ne_0^2}{\varepsilon k_\mathrm{B}T} \cdot \psi \,. \tag{3.2'}$$

Here the factor on the l.h.s. of ψ has the dimension of the reciprocal of the square of a length. We set

$$\varkappa^2 = \frac{8\pi ne_0^2}{\varepsilon k_\mathrm{B}T} \,, \tag{3.3}$$

so that $\varkappa$ is a reciprocal length, and Equation 3.2' becomes

$$\Delta\psi = \varkappa^2 \cdot \psi \,. \tag{3.4}$$

The length introduced this way

$$\boxed{\frac{1}{\varkappa} = \sqrt{\frac{\varepsilon k_\mathrm{B}T}{8\pi ne_0^2}}}$$

is the most significant quantity in our theory and replaces the mean distance between the ions in the deprecated approach of GHOSH. If one inserts numerical values (see later) and if the concentration is as usual in moles per liter of solution,

[2]We have also investigated the influence of the following terms in the development of $\sinh\left(\frac{e_0\psi}{k_\mathrm{B}T}\right)$ and found that their influence on the final result is marginal. For the sake of brevity, the communication of these calculations will be omitted.

then, if the measured concentration is denoted by γ, we have

$$\frac{1}{\varkappa} = \frac{3.06}{\sqrt{\gamma}} \cdot 10^{-8} \text{ cm}$$

for water at 0 °C. The characteristic length therefore reaches molecular dimensions when $\gamma = 1$ (1 mole per liter), see Part III.

We now wish to interrupt this course of thought in order to explore the physical meaning of the characteristic length.

In an electrolyte solution of potential 0 there is immersed an electrode whose surface has a potential difference ψ in relation to this solution. The transition from ψ to 0 will then take place in a layer of finite thickness as given by the above considerations. If we use Equation 3.4 and designate z as a coordinate perpendicular to the electrode surface, then we have

$$\psi = \Psi \cdot e^{-\varkappa \cdot z}$$

as a Ansatz that satisfies Equation 3.4[3]. Since the right-hand term of Equation 3.4 is identical to $-\frac{4\pi}{\varepsilon} \cdot \varrho$ in the sense of Poisson's equation, the charge density associated with the given potential is therefore

$$\varrho = -\frac{\varepsilon \varkappa^2}{4\pi} \cdot \psi \cdot e^{-\varkappa \cdot z} .$$

According to this formula, $\frac{1}{\varkappa}$ signifies the length at which the electric density of the ionic cloud (see Figure 3.1) decreases to the e-th part. Our characteristic length $\frac{1}{\varkappa}$ is a measure of the thickness of such an ionic cloud (i.e., of the widely known Helmholtz double layer); according to Equation 3.3 it depends on the concentration, temperature, and dielectric constant of the solvent[4].

Now that the meaning of the length $\frac{1}{\varkappa}$ has been clarified, let us now use Equation 3.4 to determine the potential and density distribution in the surrounding of the highlighted ion with the charge $+e_0$. We call the distance from this ion r and introduce spatial polar coordinates to Equation 3.4. Then Equation 3.4 becomes

$$\frac{1}{r^2} \cdot \frac{\mathrm{d}}{\mathrm{d}r} \left(r^2 \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r} \right) = \varkappa^2 \psi , \tag{3.4'}$$

[3]For the meaning or definition of the word *Ansatz* see `https://en.wikipedia.org/wiki/Ansatz`

[4]The agreement of the above results regarding the double layer with calculations of M. Gouy was subsequently shown, see [21] on the theory of the capillary electrometer. Perhaps we may point out that in this case the unabridged Equation 3.2 allows for a simple solution.

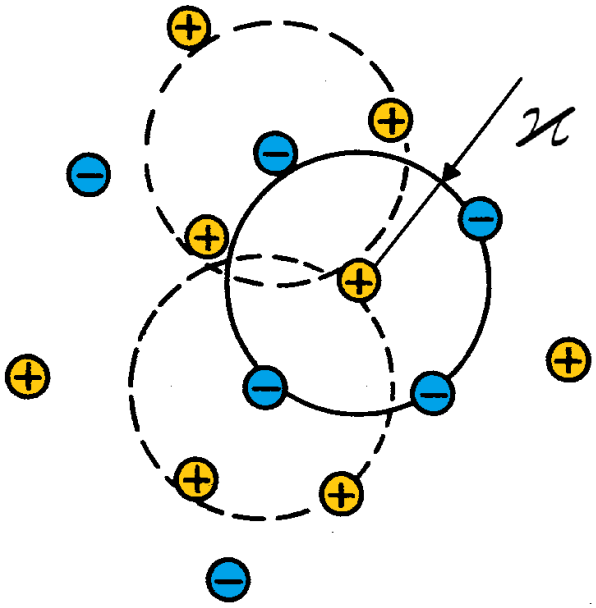

Figure 3.1.: Schematic representation of the ionic atmosphere in solution, adopted from [23]

and this equation has the general solution

$$\psi = A \cdot \frac{e^{-\varkappa \cdot r}}{r} + A' \cdot \frac{e^{\varkappa \cdot r}}{r} \,. \tag{3.5}$$

Because ψ vanishes at infinity, it follows that $A' = 0$; the constant A, on the other hand, must be determined from the conditions in the vicinity of the ion. We want to carry out this determination in two steps, section 3.1 and section 3.2, while in section 3.1 we assume that the dimensions of the ion have no effect; in section 3.2 we consider the ion to have a finite size. Considerations under section 3.1 then provide the limiting law for large dilutions, while section 3.1 subsumes the changes that are to be applied to this limiting law for larger concentrations.

3.1. Vanishing Ion Diameter

The potential of a single point charge e_0 in a medium with a dielectric constant ε would be

$$\psi = \frac{e_0}{\varepsilon} \cdot \frac{1}{r} \,,$$

if no other ions are present in the medium. Our potential according to Equation 3.5 must coincide with this expression for infinitesimally small distances, so we have

$$A = \frac{e_0}{\varepsilon}$$

and the potential wished for will be:

$$\psi = \frac{e_0}{\varepsilon} \cdot \frac{e^{-\varkappa \cdot r}}{r} = \frac{e_0}{\varepsilon} \cdot \frac{1}{r} - \frac{e_0}{\varepsilon} \cdot \frac{1 - e^{-\varkappa \cdot r}}{r} \,. \tag{3.6}$$

We have subsequently decomposed the potential into two components, the first of which represents the potential unaffected by the surrounding ions, and the second of which represents the potential originating from the ionic cloud. For small values of r, the value of this latter potential becomes equal to

$$-\frac{e_0}{\varepsilon} \cdot \varkappa \,;$$

the potential energy u, which is held by the highlighted ion $+e_0$ relative to its surrounding, is therefore[5]

$$u = -\frac{e_0^2}{\varepsilon} \cdot \varkappa \,. \tag{3.7}$$

If one now has a series of charges q_i and if the potential at the respective location of a charge is ψ_i, then according to the laws of electrostatics, the total potential energy is

$$U_e = \frac{1}{2} \cdot \sum_i q_i \cdot \psi_i \,.$$

In our case, where N positive charged ions are present, each of which has the potential difference $-\frac{e_0}{\varepsilon} \cdot \varkappa$ relative to its surrounding, and N negative charged ions with a potential difference of $+\frac{e_0}{\varepsilon} \cdot \varkappa$ are added, then the potential energy[6] wished for is

$$U_e = \frac{Ne_0}{2} \cdot \left(-\frac{e_0 \varkappa}{\varepsilon}\right) - \frac{Ne_0}{2} \cdot \left(+\frac{e_0 \varkappa}{\varepsilon}\right) = -\frac{Ne_0^2 \varkappa}{\varepsilon} \,. \tag{3.8}$$

Here, $\varkappa$ is given as a function of the concentration by Equation 3.3, so the potential energy of the ionic solution is proportional to the square root of concentration and not, as Ghosh states, proportional to the cube root of the same quantity.

[5] Apart from the graphical result mentioned in the introduction, Milner's work contains a footnote, [50], according to which, in the case of the above text, in our notation

$$u = -\frac{e_0^2}{\varepsilon} \cdot \varkappa \cdot \sqrt{\frac{\pi}{2}} \,.$$

A derivative of this formula is missing. It differs from our resultant by the factor $\sqrt{\frac{\pi}{2}}$.

[6] Because we are concerned only with the mutual potential energy, ψ_i must not take the value of the whole potential but only the part resulting from the surrounding charges, always calculated for the point at which the potential charge e_i is located.

3.2. Finite Ion Diameter

We noted earlier that the characteristic length $\frac{1}{\varkappa}$ at concentrations of $1\,\mathrm{mol\,L^{-1}}$ reaches the scale of molecular dimensions. At such concentrations, it is therefore inadmissible for the ion of finite molecular size to be replaced by a point charge, as was done under section 3.1. It would not correspond to the meaning of our calculation, based on POISSON's equation, if one would like to introduce detailed concepts about the distances of mutual approach of ions. Rather, we will now utilize a picture that considers an ion to be a sphere of radius a, whose interior is to be treated as a medium with the dielectric constant ε, and at the center of which is located the charge $+e_0$ or $-e_0$ as a point charge. The magnitude of a then does not evidently represent the ion radius but measures a length that is the mean distance up to which both surrounding positive and negative ions can approach the highlighted ion. Accordingly, with positive and negative ions of exactly equal size, a would be, for example, expected to be of the same order of magnitude as the ion diameter. In general, this ion diameter cannot yet to be regarded as the diameter of the real ion, because ions are expected to be surrounded according to their hydration by a firmly adhered layer of water molecules (hydration shell). Therefore, with the assistance of the length a, we can only approach reality in an approximative way with the schematic arguments provided above. However, the discussion of practical cases (see below) will show that this approximation is a pretty good one to a large extend.

The potential for a highlighted ion we still have

$$\psi = A \cdot \frac{e^{-\varkappa \cdot r}}{r}\,, \tag{3.9}$$

except the constant A must now be determined differently. According to our assumptions, inside the ion sphere (for a positive ion) we set

$$\psi = \frac{e_0}{\varepsilon} \cdot \frac{1}{r} + B\,. \tag{3.9'}$$

The constants A and B are to be determined from the boundary conditions at the surface of the sphere. There, i.e. for $r = a$, the potential ψ as well as the field strength $\frac{\mathrm{d}\psi}{\mathrm{d}r}$ continuously merge together.

Accordingly

$$\left.\begin{aligned} A \cdot \frac{e^{-\varkappa \cdot a}}{a} &= \frac{e_0}{\varepsilon} \cdot \frac{1}{a} + B\,, \\ A \cdot e^{-\varkappa \cdot a} \cdot \frac{1 + \varkappa a}{a^2} &= \frac{e_0}{\varepsilon} \cdot \frac{1}{a^2}\,, \end{aligned}\right\} \tag{3.10}$$

and consequently

$$\left.\begin{aligned} A &= \frac{e_0}{\varepsilon} \cdot \frac{e^{\varkappa a}}{1+\varkappa \cdot a}\,, \\ B &= -\frac{e_0 \varkappa}{\varepsilon} \cdot \frac{1}{1+\varkappa \cdot a}\,. \end{aligned}\right\} \tag{3.10'}$$

The value of B represents the potential generated at the center of the ion sphere by the ionic cloud; accordingly, one obtains the expression for the potential energy of a positive charged ion relative to its surroundings

$$u = -\frac{e_0^2 \varkappa}{\varepsilon} \cdot \frac{1}{1+\varkappa \cdot a}\,. \tag{3.11}$$

As a comparison with Equation 3.7 shows, the effect of the ion size is represented by the factor $\frac{1}{1+\varkappa \cdot a}$ only. For low concentrations (n small) $\varkappa$ is also small following Equation 3.3, and the energy approaches the value given above for infinitely small ions. For large concentrations ($\varkappa$ large), on the other hand, u gradually approaches the quantity

$$-\frac{e_0^2}{\varepsilon \cdot a}\,,$$

such that the importance of our characteristic length $\frac{1}{\varkappa}$ lessens compared to the new length a measuring the ionic size.

With the aid of Equation 3.11, the expression is similar to that under section 3.1 for the total electrical energy of the ion solution

$$U_e = -\frac{N}{2} \cdot \frac{e_0^2 \varkappa}{\varepsilon} \cdot \left[\frac{1}{1+\varkappa \cdot a_1} + \frac{1}{1+\varkappa \cdot a_2}\right], \tag{3.12}$$

if we, as it may seen obvious, characterize the positive ions by a radius a_1 and the negative ones by another radius a_2. We could now use Equation 3.8 or Equation 3.12 directly to determine our thermodynamic function as explained in chapter 2. Meanwhile, let us first derive an expression related to Equation 3.12 for the energy of an arbitrary ionic solution, by eliminating the restriction to uni-univalent salts introduced for the sake of clarity.

4. The Potential Energy of an Arbitrary Ionic Solution

In a solution there may exist

$$N_1, \dots N_i, \dots N_s$$

various kind of ions with the charges

$$z_1, \dots z_i, \dots z_s\,,$$

such that the integers $z_1, \dots z_i, \dots z_s$ can measure the valence and may be positive or negative. Because the total charge is zero,

$$\sum_i N_i z_i = 0$$

must be true. In addition to the total numbers N_i, the ion numbers per cm^3

$$n_1, \dots n_i, \dots n_s$$

are also introduced.

Again, an arbitrary ion is highlighted, and in its vicinity the potential is determined according to Poisson's equation

$$\Delta\psi = -\frac{4\pi}{\varepsilon} \cdot \varrho\,.$$

The density of ions of the i-th kind is determined by Boltzmann's principle

$$n_i \cdot e^{-z_i \cdot \frac{e_0 \psi}{k_\mathrm{B} T}}\,,$$

such that

$$\varrho = e_0 \cdot \sum_i n_i z_i \cdot e^{-z_i \cdot \frac{e_0 \psi}{k_\mathrm{B} T}}$$

and the fundamental equation becomes

$$\Delta\psi = -\frac{4\pi e_0}{\varepsilon} \cdot \sum_i n_i z_i \cdot e^{-z_i \cdot \frac{e_0 \psi}{k_B T}} . \tag{4.1}$$

If we use the expansion of the exponential function as in the previous paragraph, then Equation 4.1 practically turns into the equation

$$\Delta\psi = -\frac{4\pi e_0^2}{\varepsilon k_B T} \cdot \sum_i n_i z_i^2 \psi , \tag{4.1'}$$

because the condition

$$\sum_i n_i z_i = 0$$

causes the first term of the expansion to vanish. In the general case, therefore, the square of our characteristic length $\frac{1}{\varkappa^2}$ is to be defined by the equation[1]

$$\varkappa^2 = \frac{4\pi e_0^2}{\varepsilon k_B T} \cdot \sum_i n_i z_i^2 , \tag{4.2}$$

while the equation for the electric potential maintains its former form

$$\Delta\psi = \varkappa^2 \cdot \psi .$$

Again, a random ion is highlighted and the potential ψ in its vicinity is determined. In accordance with the statements of the previous paragraph, it is

$$\psi = A \cdot \frac{e^{-\varkappa \cdot r}}{r}$$

for the field outside the ion.

If the ion has the charge $z_i \cdot e_0$ and does it show an approach distance of a_i, then for the inside of the ionic sphere we get

$$\psi = \frac{z_i e_0}{\varepsilon} \cdot \frac{1}{r} + B ,$$

[1] Because, for monovalent salts, $n_1 = n_2 = n$ and $z_1 = z_2 = 1$, the general Equation 4.2 for $\varkappa^2$ agrees with the earlier one (see Equation 3.3) given for this special case.

while the constants A and B result in

$$A = \frac{z_i e_0}{\varepsilon} \cdot \frac{e^{\varkappa \cdot a_i}}{1 + \varkappa \cdot a_i},$$
$$B = -\frac{z_i e_0 \varkappa}{\varepsilon} \cdot \frac{1}{1 + \varkappa \cdot a_i}.$$

The given value of B corresponds to the potential energy

$$u = -\frac{z_i^2 e_0^2 \varkappa}{\varepsilon} \cdot \frac{1}{1 + \varkappa \cdot a_i}$$

of the highlighted ion relative to its ionic cloud, while the total electrical energy of the ion solution, as can be readily seen, is

$$U_e = -\sum_i \frac{N_i z_i^2}{2} \cdot \frac{e_0^2 \varkappa}{\varepsilon} \cdot \frac{1}{1 + \varkappa \cdot a_i}. \tag{4.3}$$

The inverse length $\varkappa$ is defined in the general case by Equation 4.2[2].

[2]By the expression given for U_e, we are immediately able to derive to the heat of dilution. We convinced ourselves that the theoretical value corresponds to the observations.

5. The Additional Electric Term to the Thermodynamic Potential

In section 2.1 we came to the conclusion that the additional term originating in the potential from the mutual effect of the ions

$$G = S - \frac{U}{T}$$

was to be determined from the equation

$$G_e = \int \frac{U_e}{T^2}\,\mathrm{d}T\,.$$

If we now use the expression given in Equation 4.3 for U_e to immediately address the general case, it must be remembered when integrating that according to Equation 4.2 the reciprocal length in this expression contains the temperature. The calculation becomes clearer when we first conclude from Equation 4.2 that

$$2\varkappa\,\mathrm{d}\varkappa = -\frac{4\pi e_0^2}{\varepsilon k_\mathrm{B}} \cdot \sum_i n_i z_i^2 \cdot \frac{\mathrm{d}T}{T^2}\,,$$

where ε is considered to be temperature-independent[1], and then use $\varkappa$ as the integration variable, not T. So the result is

$$G_e = \frac{k_\mathrm{B}}{4\pi \cdot \sum_i n_i z_i^2} \cdot \sum_i N_i z_i^2 \cdot \int \frac{\varkappa}{1 + \varkappa \cdot a_i}\,\mathrm{d}\varkappa\,. \tag{5.1}$$

If one applies the abbreviation

$$\varkappa \cdot a_i = x_i \tag{5.2}$$

[1] In fact, a direct kinetic theory of osmotic pressure, reported elsewhere (*Recueil des travaux chimiques des Pays-Bas et de la Belgique*), shows the validity of the final expression for G_e independent of this assumption. For a discussion of the thermodynamic calculation we can refer to B. A. M. Cavanagh, [11].

one finds that

$$\int^{\varkappa=x} \frac{\varkappa^2\,\mathrm{d}\varkappa}{1+\varkappa\cdot a_i} = \frac{1}{a_i^3}\cdot\int^{u=x_i}\frac{u^2\,\mathrm{d}u}{1+u}$$
$$= \frac{1}{a_i^3}\cdot\left\{\text{const.}+\log(1+x_i)-2\cdot(1+x_i)+\frac{1}{2}\cdot(1+x_i)^2\right\}.$$

The constant of integration is determined in such a way that the electric addition G_e to the total potential vanishes in the limit for infinitesimal dilution. Because $\varkappa$ in Equation 4.2 is proportional to $\sqrt{\sum_i n_i z_i^2}$, $\varkappa = 0$ corresponds to the case of infinitesimal dilution. Accordingly, the constant in the curly brace must be determined such that for $x_i = 0$ the parenthetical expression also vanishes, and because within that limit

$$\log(1+x_i)-2\cdot(1+x_i)+\frac{1}{2}\cdot(1+x_i)^2$$

takes on the value $-\frac{3}{2}$, it follows that

$$\text{const.} = \frac{3}{2}$$

has to be set. With this it follows that

$$\int\frac{\varkappa^2\,\mathrm{d}\varkappa}{1+\varkappa\cdot a} = \frac{1}{a_i^3}\cdot\left\{\frac{3}{2}+\log(1+x_i)-2\cdot(1+x_i)+\frac{1}{2}\cdot(1+x_i)^2\right\}$$

and

$$\left.\begin{aligned} G_e &= \frac{k_\mathrm{B}}{4\pi\cdot\sum_i n_i z_i^2}\cdot\sum_i\frac{N_i z_i^2}{a_i^3} \\ &= \cdot\left\{\frac{3}{2}+\log(1+x_i)-2\cdot(1+x_i)+\frac{1}{2}\cdot(1+x_i)^2\right\}. \end{aligned}\right\} \tag{5.3}$$

The function in the curly brace, when expanded in powers of x_i, takes the form

$$\frac{3}{2}+\log(1+x_i)-2\cdot(1+x_i)+\frac{1}{2}\cdot(1+x_i)^2 = \frac{x_i^3}{3}-\frac{x_i^4}{4}+\frac{x_i^5}{5}-\frac{x_i^6}{6}+\cdots;$$

if one therefore sets the abbreviation

$$\chi_i = \chi(x_i) = \frac{3}{x_i^3}\cdot\left\{\frac{3}{2}+\log(1+x_i)-2\cdot(1+x_i)+\frac{1}{2}\cdot(1+x_i)^2\right\}, \tag{5.4}$$

χ approaches the value 1 for small concentrations and can be expanded to give

$$\chi_i = 1 - \frac{3}{4} \cdot x_i + \frac{3}{5} \cdot x_i^2 - \cdots . \tag{5.4'}$$

By introducing this function and considering the definition in Equation 4.2 for $\varkappa^2$, our addition to the thermodynamic potential can be reduced to the form[2]

$$G_e = \sum_i N_i \cdot \frac{z_i^2 e_0^2}{\varepsilon T} \cdot \frac{\varkappa}{3} \cdot \chi_i \,, \tag{5.5}$$

where, for the sake of clarity, according to Equation 4.2 for $\varkappa$,

$$\varkappa^2 = \frac{4\pi e_0^2}{\varepsilon k_\mathrm{B} T} \cdot \sum_i n_i z_i^2$$

is explicitly repeated again here.

For small concentrations, therefore, in G_e, each ion has a contribution proportional to $\varkappa$, i.e. proportional to the square root of the concentration. If the finite dimensions of the ions were neglected, then, according to Equation 5.4' and Equation 5.2, χ_i would have to be set equal to 1 in any case, and this dependency would appear to be valid for all concentrations. The dependence on the ion's size, which takes into account the individual properties of the ions, is therefore measured by the function χ given by Equation 5.4 or Equation 5.4'. In the limit for large dilutions, however, this influence vanishes, and the ions only differ as far as their valences are different.

[2]The additional electric pressure p_e, which was mentioned in section 2.1, Equation 2.6', results from this formula. The numerical value given there was calculated in this way.

6. Osmotic Pressure, Vapor Pressure Depression, Freezing-Point Depression, Boiling-Point Elevation

According to section 2.1 regarding equations Equation 2.7, Equation 2.7', and Equation 2.7", the thermodynamic function Φ of the solution is represented by the expression

$$\Phi = \sum_{i=0}^{s} N_i \cdot [\varphi_i - k_\mathrm{B} \cdot \log(c_i)] + \sum_{i=1}^{s} N_i \cdot \frac{z_i^2 e_0^2}{3\varepsilon} \cdot \frac{\varkappa}{T} \cdot \chi_i \,. \tag{6.1}$$

In this case, for the electric addition to Φ, Equation 5.5 is used, in which $\chi_i = \chi(x_i) = \chi(\varkappa a_i)$ is given by Equation 5.4 and, as explained in the previous paragraph, approaches the value of 1 (unity) in the limit for infinitesimal concentrations. $\varkappa$ is our reciprocal characteristic length, defined by Equation 4.2, according to which

$$\varkappa^2 = \frac{4\pi e_0^2}{\varepsilon k_\mathrm{B} T} \cdot \sum_i n_i z_i^2 \,.$$

According to the method used in Planck's textbook on thermodynamics, the laws of the phenomena named in the heading can all be deduced by differentiation of Equation 6.1. The condition for equilibrium in the case of transition of a quantity of δN_0-molecules of the solvent from the solution to the respective other phase is known to be

$$\delta\Phi + \delta\Phi' = 0 \,,$$

if Φ' signifies the thermodynamic potential of that second phase. We set

$$\Phi' = N_0' \cdot \varphi_0' \tag{6.2}$$

and wish to account for the case of equilibrium between the solution and the frozen solvent, bearing in mind that the most extensive and reliable measurements exist for freezing-point depression as a function of concentration. We now let N_0 vary

by δN_0 and N_0' vary by $\delta N_0'$ and then immediately find that

$$\begin{aligned}\delta\left(\Phi+\Phi'\right) &= \varphi_0'\delta N_0' + \left[\varphi_0 - k_\mathrm{B}\cdot\log(c_0)\right]\delta N_0 \\ &\quad + \sum_{i=1}^{s} N_i\cdot\frac{z_i^2e_0^2}{3\varepsilon T}\cdot\frac{\mathrm{d}(\varkappa\chi_i)}{\mathrm{d}\varkappa}\cdot\frac{\partial\varkappa}{\partial N_0}\cdot\delta N_0\,,\end{aligned} \tag{6.3}$$

as it is easily apparent that

$$\sum_{i=0}^{s} N_i\delta\log(c_i) = \sum_{i=0}^{s} N_i\cdot\frac{\partial\log(c_i)}{\partial N_0}\delta N_0$$

has the value zero.

Because

$$\delta N_0' = -\delta N_0\,,$$

the condition for equilibrium is

$$\varphi_0' - \varphi_0 = -k_\mathrm{B}\cdot\log(c_0) + \sum_{i=1}^{s} N_i\cdot\frac{z_i^2e_0^2}{3\varepsilon T}\cdot\frac{\mathrm{d}(\varkappa\chi_i)}{\mathrm{d}\varkappa}\cdot\frac{\partial\varkappa}{\partial N_0}\,; \tag{6.4}$$

This equation could be utilized in this form for all the phenomena named in the heading and represents a relation between pressure, temperature, and concentrations.

In the definition of $\varkappa$, n_i represents the number of ions of the i-th type per unit volume, such that

$$n_i = \frac{N_i}{V}\,.$$

On the other hand, the linear Ansatz,

$$V = \sum_{i=0}^{s} n_iv_i = n_0v_0 + \sum_{i=1}^{s} n_iv_i$$

like the one used by Planck for the volume V, is applied for the whole formulation. According to Equation 4.2 it therefore results

$$\begin{aligned}2\varkappa\cdot\frac{\partial\varkappa}{\partial N_0} &= -\frac{4\pi e_0^2}{\varepsilon k_\mathrm{B}T}\cdot\sum_i z_i^2\cdot\frac{N_iv_0}{V^2} \\ &= -\frac{4\pi e_0^2}{\varepsilon k_\mathrm{B}T}\cdot\frac{v_0}{V}\cdot\sum_i n_iz_i^2\,;\end{aligned}$$

x	$\sigma(x)$	x	$\sigma(x)$	x	$\sigma(x)$	x	$\sigma(x)$
0	1.000	0.4	0.598	0.9	0.370	3.0	0.1109
0.05	0.929	0.5	0.536	1.0	0.341	3.5	0.0898
0.1	0.855	0.6	0.486	1.5	0.238	4.0	0.0742
0.2	0.759	0.7	0.441	2.0	0.176	4.5	0.0628
0.3	0.670	0.8	0.403	2.5	0.136	5.5	0.0540

Table 6.1.: Numerical values for $\sigma(x)$

by taking into account this defining equation again one obtains

$$\frac{\partial \varkappa}{\partial N_0} = -\frac{\varkappa}{2} \cdot \frac{v_0}{V} ,$$

and our condition for equilibrium takes the form:

$$\varphi_0 - \varphi_0' = k_\mathrm{B} \cdot \log(c_0) + v_0 \cdot \sum_{i=1}^{s} n_i \cdot \frac{z_i^2 e_0^2}{6\varepsilon T} \cdot \varkappa \cdot \frac{\mathrm{d}(\varkappa \chi_i)}{\mathrm{d}\varkappa} . \tag{6.4'}$$

The function for concentration characterizing the effects in question

$$\frac{\mathrm{d}(\varkappa \chi_i)}{\mathrm{d}\varkappa}$$

can easily be calculated from Equation 5.4. If we designate it as σ_i, it follows while keeping the abbreviation

$$x_i = \varkappa \cdot a_i$$

as

$$\begin{aligned} \sigma_i &= \frac{\mathrm{d}(\varkappa \chi_i)}{\mathrm{d}\varkappa} \\ &= \frac{3}{x_i^3} \cdot \left[(1 + x_i) - \frac{1}{(1 + x_i)} - 2 \cdot \log(1 + x_i) \right] . \end{aligned} \tag{6.5}$$

For small values of x_i, the following expansion applies,

$$\sigma_i = 1 - \frac{3}{2} x_i + \frac{9}{5} x_i^2 - 2 x_i^3 + \cdots = \sum_{\nu=0}^{\nu=s} 3 \cdot \frac{\nu + 1}{\nu + 3} \cdot x_i^\nu ,$$

such that σ_i approaches the value 1 (unity) for small concentrations; for large concentrations, σ_i vanishes as $\frac{3}{x_i^2}$. Table 6.1 contains numerical values for σ as a function of $x = \varkappa \cdot a$; Figure 6.1 presents the trend of the function graphically.

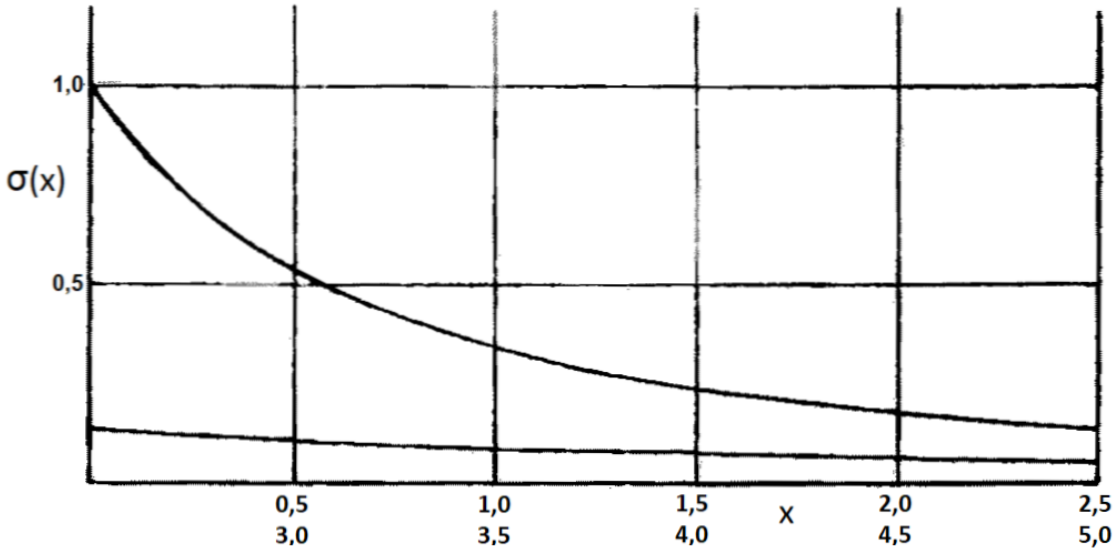

Figure 6.1.: Graphical representation of the dependence of $\sigma(x)$ from x

Because we will later take the opportunity to address the freezing-point of concentrated solutions, it is advisable to calculate the magnitude of depression from Equation 6.4' without first introducing all the simplifications that are permitted in very dilute solutions. The freezing-point of the pure solvent shall be T_0, the freezing-point of the solution $T_0 - \Delta$, the heat of fusion of the frozen solvent H_{fus}, the specific heat capacity of the liquid solvent at constant pressure c_p, and the same quantity for the frozen solvent c'_p. The three latter quantities should always be related to a real molecule, such that they represent the typical molar quantities divided by AVOGADRO's constant. Then, according to the equation that defines φ, we have

$$\varphi_0 - \varphi'_0 = -\frac{\Delta}{T_0} \cdot \frac{H_{\text{fus}}}{T_0} + \frac{\Delta^2}{T_0^2} \cdot \left[\left(c_p - c'_p \right) - \frac{2H_{\text{fus}}}{k_{\text{B}} T} \right] .$$

For c_0 we can insert

$$c_0 = 1 - \sum_{i=1}^{s} c_i \, .$$

Because we further set

$$\frac{\mathrm{d}(\varkappa \chi_i)}{\mathrm{d}\varkappa} = \sigma_i$$

it finally follows that

$$\begin{aligned} &\frac{\Delta}{T_0} \cdot \frac{H_{\text{fus}}}{k_{\text{B}} T_0} - \frac{\Delta^2}{T_0^2} \cdot \left[\frac{c_p - c'_p}{2k_{\text{B}}} - \frac{H_{\text{fus}}}{k_{\text{B}} T_0} \right] \\ &= -\log \left(1 - \sum_{i=1}^{s} c_i \right) - \frac{e_0^2 \varkappa}{6\varepsilon k_{\text{B}} T} \cdot \sum_{i=1}^{s} v_0 n_i z_i^2 \sigma_i \, . \end{aligned}$$

If AVOGADRO's constant N_A is introduced, then

$$N_A \cdot H_{\text{fus}} = Q$$

is the melting heat of one mole,

$$N_A \cdot k_{\text{B}} = \mathscr{R}$$

is the gas constant, and

$$N_A \cdot c_p = C_p \quad \text{and} \quad N_A \cdot c'_p = C'_p$$

the specific heat per mole of liquid or solid solvent, respectively, such that one can also write

$$\left.\begin{aligned} &\frac{\Delta}{T_0} \cdot \frac{Q}{\mathscr{R}\, T_0} - \frac{\Delta^2}{T_0^2} \cdot \left[\frac{C_p - C'_p}{2\,\mathscr{R}} - \frac{Q}{\mathscr{R}\, T_0}\right] \\ &= -\log\left(1 - \sum_{i=1}^{s} c_i\right) - \frac{e_0^2 \varkappa}{6\varepsilon k_{\text{B}} T} \cdot \sum_{i=1}^{s} v_0 n_i z_i^2 \sigma_i \,. \end{aligned}\right\} \tag{6.6}$$

For small concentrations, firstly, $\frac{\Delta^2}{T_0^2}$ can be neglected next to $\frac{\Delta}{T_0}$, secondly,

$$-\log\left(1 - \sum_{i=1}^{s} c_i\right) = \sum_{i=1}^{s} c_i$$

can be set, and thirdly, the total volume can be identified with the volume of water by considering the number of dissolved ions as infinitesimal relative to the number of water molecules. It therefore is identical when we set

$$v_0 n_i = \frac{v_0}{V} \cdot N_i = \frac{N_i}{N_0} = \frac{N_i}{N_0 + \sum_{i=1}^{s} v_i N_i} = c_i \,.$$

With these approximations one finds[1]

$$\frac{\Delta}{T_0} \cdot \frac{Q}{\mathscr{R}\, T_0} = \sum_{i=1}^{s} c_i \cdot \left(1 - \frac{e_0^2 \varkappa}{6\varepsilon k_{\text{B}} T} \cdot z_i^2 \sigma_i\right) , \tag{6.7}$$

whereas with the same assumptions, the classical formula will be

$$\frac{\Delta}{T_0} \cdot \frac{Q}{\mathscr{R}\, T_0} = \sum_{i=1}^{s} c_i \,. \tag{6.7'}$$

[1]There is no need to make a distinction between ions and uncharged molecules; if both occur, one simply has to set $z_i = 0$ for the latter. If all particles are uncharged, naturally Equation 6.7 and Equation 6.7' become identical.

7. The Freezing-Point Depression of Dilute Solutions

The characteristics of the electrical effect of the ions are particularly evident in the limiting laws for large dilutions, as represented by Equation 6.7. We therefore wish to treat these formulæ and laws for this limiting case separately. Equation 6.7 is applicable to the general case of a mixture of a variety of electrolytes that may also have only partially dissociated into ions. Here we consider the special case of a single species of molecule dissolved in the solution. The molecule may be completely dissociated into ions and consists of s-ion species, numbered $1, \ldots, i, \ldots s$, such that

$$\nu_1, \ldots \nu_i, \ldots \nu_s$$

ions of the species $1, \ldots, i, \ldots s$ constitute the molecule. The charges associated with each of these ions are

$$z_1 e_0, \ldots z_i e_0, \ldots z_s e_0 \,.$$

(For H_2SO_4, dissociated into the ions H^+ and $SO_4{}^{2-}$, this will be for example,

$$\nu_1 = 2\,, \quad \nu_2 = 1\,, \quad z_1 = +1\,, \quad z_2 = -2\,,$$

if the subscript index 1 is related to the H-ions and the subscript index 2 to the SO_4-ions.)

Because the molecule as a whole is uncharged, the following holds:

$$\sum_{i=1}^{s} \nu_i z_i = 0\,.$$

The solution may now consist of N_0 molecules of solvent and N molecules of the added electrolyte, whereby N is considered small relative to N_0. Then,

$$c_i = \frac{N_i}{N_0 + \sum_{i=1}^{s} N_i} = \frac{N_i}{N_0}\,.$$

Considering that

$$N_i = \nu_i \cdot N_A$$

and designating c as the concentration of the dissolved species, so that the approximation used here becomes

$$c = \frac{N_A}{N_0}\,,$$

it follows that

$$c_i = \nu_i \cdot c\,.$$

Equation 6.7 for the freezing-point depression then becomes

$$\frac{\Delta}{T_0} \cdot \frac{Q}{\mathscr{R}\,T_0} = f_0 \cdot \sum_i c_i = f_0 c \cdot \sum_i \nu_i \tag{7.1}$$

with

$$f_0 = 1 - \frac{e_0^2 \varkappa}{6\varepsilon k_\mathrm{B} T} \cdot \frac{\sum_i \nu_i z_i^2 \sigma_i}{\sum_i \nu_i}\,. \tag{7.2}$$

The quantity f_0 is the osmotic coefficient mentioned in the introduction, because $f_0 = 1$ would correspond to the transition to classical theory, as shown by Equation 6.7'. If one calls Δ_k the freezing-point depression calculated according to the classical theory, then

$$\frac{\Delta}{\Delta_k} = f_0$$

or

$$1 - f_0 = \frac{\Delta_k - \Delta}{\Delta_k}\,.$$

Equation 7.2 therefore shows, qualitatively for the moment, that the actual depression of the freezing-point must be smaller than expected under classical theory, a result that is in every way confirmed for dilute electrolyte solutions. The quantities $\varkappa$ and σ occurring in Equation 7.2 are determined by Equation 4.2 and Equation 6.5 (the latter with the associated table). As explained in the previous section, σ_i measures the influence of the finite ionic size and vanishes at very low concentrations, because then σ tends to the value 1. Accordingly, if we deal first with the limiting law, which should be valid for very large dilutions, then in the limiting case we find

$$f_0 = 1 - \frac{e_0^2 \varkappa}{6\varepsilon k_\mathrm{B} T} \cdot \frac{\sum_i \nu_i z_i^2}{\sum_i \nu_i}\,. \tag{7.3}$$

On the other hand, according to Equation 4.2

$$\varkappa^2 = \frac{4\pi e_0^2}{\varepsilon k_\mathrm{B} T} \cdot \sum_i n_i z_i^2\,;$$

however, because

$$n_i = \nu_i \cdot \frac{N_A}{V} = \nu_i n$$

with the introduction of the volume concentration n of the dissolved molecules, so too

$$\varkappa^2 = \frac{4\pi n e_0^2}{\varepsilon k_\mathrm{B} T} \cdot \sum_i \nu_i z_i^2 \,.$$

It follows that for very low concentrations,

$$f_0 = 1 - \frac{e_0^2}{6\varepsilon k_\mathrm{B} T} \cdot \sqrt{\frac{4\pi e_0^2}{\varepsilon k_\mathrm{B} T} \cdot n \cdot \sum_i \nu_i} \cdot \left(\frac{\sum_i \nu_i z_i^2}{\sum_i \nu_i} \right)^{\frac{3}{2}} \,, \tag{7.3'}$$

where $n \cdot \sum_i \nu_i$ represents the total number of ions per cm^3 of the solution, and

$$w = \left(\frac{\sum_i \nu_i z_i^2}{\sum_i \nu_i} \right)^{\frac{3}{2}} \tag{7.4}$$

is to be called the valence factor, because it measures the influence of the ion valences z_i regarding these phenomena. It is best not to consider f_0 itself but the deviation from 1 (unity) and so write for very low concentrations:

$$1 - f_0 = w \cdot \frac{e_0^2}{6\varepsilon k_\mathrm{B} T} \cdot \sqrt{\frac{4\pi e_0^2}{\varepsilon k_\mathrm{B} T} \cdot n \cdot \sum_i \nu_i} \,. \tag{7.5}$$

At first, this formula expresses how the deviations $1 - f_0$ depend on the concentration, namely, it states in this regard:

Proof. For all electrolytes, in the limit for low concentrations, the percentage deviation of the freezing-point depression from the classical value is proportional to the square root of the concentration. □

That it is possible to state this law as a general law is, because all the electrolytes for large dilutions can be considered as completely dissociated into ions. Of course, only the strong electrolytes practically reach that area of complete dissociation.

Secondly, Equation 7.4 makes a statement about the influence of ion valence, which can be formulated as follows:

Proof. If the dissolved molecule dissociates into $\nu_1, \ldots \nu_i, \ldots \nu_s$ different ions of types $1, \ldots i, \ldots s$ with the valences $z_1, \ldots z_i, \ldots z_s$, then, for low concentrations, the percentage deviation of the freezing-point depression from the classical value is proportional to a valence factor w, which is calculated according to

$$w = \left(\frac{\sum_i \nu_i \cdot z_i^2}{\sum_i \nu_i} \right)^{\frac{3}{2}} \,.$$

□

Type	Valence factor, w
KCl	$1 = 1$
$CaCl_2$ ...	$2 \cdot \sqrt{2} = 2,83$
$CuSO_4$...	$4 \cdot \sqrt{4} = 8$
$AlCl_3$....	$3 \cdot \sqrt{3} = 5,20$
$Al_2(SO_4)_3$	$6 \cdot \sqrt{6} = 16,6$

Table 7.1.: Valence factor w of different salts

As an example for the calculation of this valence factor, Table 7.1 is presented, where in the left column an example of the type of salt is given, and in the right column the value of w is given:

The influence of the ions therefore increases considerably with increasing valence, which also corresponds to the qualitative findings.

Thirdly, the solvent has an influence, in the sense of NERNST's well-known suggestion for explaining the ionizing force of solvents with a high dielectric constant. Following Equation 7.5, one finds

Proof. For low concentrations, the percentage deviation of the freezing point depression from the classical value is inversely proportional to the 3/2th power of the dielectric constant of the solvent. □

The remaining constants in Equation 7.5 are the charge of the elementary electric quantum $e_0 = 4.77 \times 10^{-10}$ e.s.u. (or $1.602\,176\,63 \times 10^{-19}$ C), BOLTZMANN's constant $k_B = 1.346 \times 10^{-16}\,\mathrm{erg\,Grad^{-1}}$ (or $1.380\,649 \times 10^{-23}\,\mathrm{J\,K^{-1}}$), and the temperature T, the latter of which occurs both explicitly and implicitly, because the dielectric constant ε varies with T.

If one deals with dilute solutions in the conventional sense, then σ can no longer be replaced by 1 (unity), and Equation 7.2 comes into effect, which is explicitly:

$$1 - f_0 = w \cdot \frac{e_0^2}{6\varepsilon k_B T} \cdot \sqrt{\frac{4\pi e_0^2}{\varepsilon k_B T} \cdot n \cdot \sum_i \nu_i} \cdot \frac{\sum_i \nu_i z_i^2 \sigma_i}{\sum_i \nu_i z_i^2}\,. \tag{7.6}$$

As Table 6.1 shows, as well as Equation 6.5, upon which it is based, σ_i continuously decreases with increasing concentration, and ultimately like

$$\frac{3}{x_i^2} = \frac{3}{\varkappa^2 a_i^2},$$

i.e. inversely proportional to the concentration, because $\varkappa$ is proportional to the square root of this quantity. Therefore, according to Equation 7.6, the deviation $1 - f_0$ must first increase proportional to the square root of the concentration for very low concentrations but then reach a maximum with increasing concentration in view of the influence of σ, i.e. in view of the influence of the finite diameter of the ions and finally decrease again inversely proportional to the square root of the concentration. Although this statement contains a poorly justified extrapolation to larger concentrations of Equation 7.6, which is devoted to dilute solutions, the statement remains qualitatively valid even on closer examination of more concentrated solutions (see chapter 9). In fact, the measurements also have shown a maximum of the deviation $1 - f_0$ as a characteristic of the curves for the freezing-point depression. However, we believe that the phenomena of hydration (see the concluding section) also significantly influences the creation of the maximum. A numerical comparison of the theory with empirical knowledge will be provided in chapter 9.

8. The Dissociation Equilibrium

If one does not restrict oneself only to strong electrolytes, there will be an equilibrium of dissociation between undissociated molecules and ions. However, this equilibrium will not be calculated according to the classical formula, because likewise the mutual electrical forces of the ions will interfere. The way in which this happens quantitatively according to our theory will be calculated here. We start again from Equation 6.1 for the thermodynamic potential Φ of the solution

$$\Phi = \sum_{i=0}^{s} N_i \cdot [\varphi_i - k_\mathrm{B} \cdot \log(c_i)] + \sum_{i=1}^{s} N_i \cdot \frac{z_i^2 e_0^2}{3\varepsilon} \cdot \frac{\varkappa}{T} \cdot \chi_i \,;$$

between the individual particles which are present in the solution, which are both charged and uncharged. For the latter we simply have to set $z_i = 0$. The solvent will be provided with the subscript index $_0$. Now we introduce a variation of the number N_i in the well-known manner and calculate the corresponding change of the potential. This results in

$$\begin{aligned}\delta\Phi = &\sum_{i=0}^{i=s} \delta N_i \cdot [\varphi_i - k_\mathrm{B} \cdot \log(c_i)] + \sum_{i=1}^{i=s} \delta N_i \cdot \frac{z_i^2 e_0^2}{3\varepsilon} \cdot \frac{\varkappa}{T} \cdot \chi_i \\ &+ \sum_{i=1}^{i=s} N_i \cdot \frac{z_i^2 e_0^2}{3\varepsilon T} \cdot \frac{\mathrm{d}(\varkappa\chi_i)}{\mathrm{d}\varkappa} \cdot \sum_{j=1}^{j=s} \frac{\partial\varkappa}{\partial N_j} \cdot \delta N_j \,,\end{aligned}$$

if we take into account that, according to the defining Equation 4.2

$$\varkappa^2 = \frac{4\pi e_0^2}{\varepsilon k_\mathrm{B} T} \cdot \sum_{l=1}^{l=s} n_l z_l^2 = \frac{4\pi e_0^2}{\varepsilon k_\mathrm{B} T} \cdot \sum_{l=1}^{l=s} \frac{N_l z_l^2}{V} \,;$$

the quantity $\varkappa$ may depend on all numbers $N_1, \ldots N_s$. If one changes the indices of summation i and j in the third sum, then $\delta\Phi$ may also be brought to the form:

$$\begin{aligned}\delta\Phi = \delta N_0 \cdot [\varphi_0 - k_\mathrm{B} \cdot \log(c_0)] + \sum_{i=1}^{i=s} \delta N_i \cdot \Bigg\{ &\varphi_i - k_\mathrm{B} \cdot \log(c_i) \\ &+ \frac{e_0^2}{3\varepsilon T} \cdot \left(z_i^2 \varkappa\chi_i + \sum_{j=1}^{j=s} N_j z_j^2 \cdot \frac{\mathrm{d}(\varkappa\chi_j)}{\mathrm{d}\varkappa} \cdot \frac{\partial\varkappa}{\partial N_i} \cdot \delta N_j \right) \Bigg\} \,.\end{aligned}$$

However, following the definition of $\varkappa$, $\frac{\partial \varkappa}{\partial N_i}$ can be calculated. If, for the volume the linear approach is maintained, we have

$$\frac{\partial \varkappa}{\partial N_i} = \frac{\varkappa}{2 \cdot \sum_{l=1}^{s} n_l z_l^2} \cdot \frac{z_i^2 - v_i \cdot \sum_{l=1}^{s} n_l z_l^2}{V} .$$

Making the conventional assumption that a chemical reaction takes place in the solution at which the following proportion holds good

$$\delta N_1 : \delta N_2 : \ldots : \delta N_i : \ldots : \delta N_s = \mu_1 : \mu_2 : \ldots : \mu_i : \ldots \mu_s ,$$

the equilibrium condition follows from the specified value of the variation of the potential

$$\left.\begin{aligned} \sum_{i=1}^{i=s} \mu_i \cdot \log(c_i) = \sum_{i=1}^{i=s} \frac{\mu_i \varphi_i}{k_\mathrm{B}} \\ + \frac{e_0^2 \varkappa}{6\varepsilon k_\mathrm{B} T} \cdot \sum_{i=1}^{i=s} \left\{ 2\mu_i z_i^2 \chi_i + \mu_i \cdot \left(z_i^2 - v_i \cdot \sum_{j=1}^{s} n_j z_j^2 \right) \right. \\ \left. \cdot \frac{\sum_{j=1}^{j=s} n_j z_j^2 \cdot \frac{\mathrm{d}(\varkappa \chi_j)}{\mathrm{d}\varkappa}}{\sum_{j=1}^{j=s} n_j z_j^2} \right\} . \end{aligned}\right\} \quad (8.1)$$

This differs from the classical condition by the additional term on the right-hand side. If one introduces the activity coefficient f_a, as was done in the introduction, by setting

$$\sum_{i=1}^{s} \mu_i \cdot \log(c_i) = \log(f_a \cdot K) ,$$

where K is the classical equilibrium constant, the activity coefficient is defined by the relationship

$$\left.\begin{aligned} \log(f_a) = \frac{e_0^2 \varkappa}{6\varepsilon k_\mathrm{B} T} \cdot \sum_{i=1}^{i=s} \left\{ 2\mu_i z_i^2 \chi_i \right. \\ \left. + \mu_i \cdot \left(z_i^2 - v_i \cdot \sum_{j=1}^{j=s} n_j z_j^2 \right) \cdot \frac{\sum_{j=1}^{j=s} n_j z_j^2 \cdot \frac{\mathrm{d}(\varkappa \chi_j)}{\mathrm{d}\varkappa}}{\sum_{j=1}^{j=s} n_j z_j^2} \right\} . \end{aligned}\right\} \quad (8.2)$$

According to this formula, it is of course possible to assign each atom participating in the reaction or molecule with its own activity coefficient by setting

$$\log(f_a) = \mu_1 \cdot \log(f_a^1) + \cdots + \mu_i \cdot \log(f_a^i) + \cdots + \mu_s \cdot \log(f_a^s) \quad (8.3)$$

with

$$\log(f_a^i) = \frac{e_0^2 \varkappa}{6\varepsilon k_\mathrm{B} T} \cdot \left\{ 2z_i^2 \chi_i + \left(z_i^2 - v_i \cdot \sum_{j=1}^{s} n_j z_j^2 \right) \cdot \frac{\sum_{j=1}^{j=s} n_j z_j^2 \cdot \frac{\mathrm{d}(\varkappa \chi_j)}{\mathrm{d}\varkappa}}{\sum_{j=1}^{j=s} n_j z_j^2} \right\} . \tag{8.3'}$$

But then, as Equation 8.3' shows through the occurrence of $\varkappa$, this coefficient related to a specific type of atom does not only depend on quantities that relate to that type of atom alone.

Again, simplifications are possible when limited to smaller concentrations. In that case,

$$v_i \cdot \sum_{j=1}^{s} n_j z_j^2$$

can be neglected compared to z_i^2; when this is done, the volume of the dissolved substance is regarded as vanishing with respect to the volume of the whole solution. Therefore,

$$\log(f_a^i) = \frac{e_0^2 \varkappa}{6\varepsilon k_\mathrm{B} T} \cdot z_i^2 \cdot \left\{ 2\chi_i + \frac{\sum_{j=1}^{j=s} n_j z_j^2 \cdot \frac{\mathrm{d}(\varkappa \chi_j)}{\mathrm{d}\varkappa}}{\sum_{j=1}^{j=s} n_j z_j^2} \right\} . \tag{8.4}$$

Finally, the limit can be specified the activity coefficient tends to for maximally diluted solutions. In this limit, where the effect of ion's size vanishes, $\chi = 1$ can be set to obtain

$$\log(f_a^i) = \frac{e_0^2 \varkappa}{2\varepsilon k_\mathrm{B} T} \cdot z_i^2 \, . \tag{8.5'}$$

Because $\varkappa$ depends on the properties of all ions (affected by their valence), even in this limit, the single coefficient f_a^i is not simply a function of the properties of the i-th ion. We refrain from discussing the limiting law in detail and only comment again that, in the limit, $\log(f_a)$ is proportional to the square root of the concentration.

9. Comparison of Freezing-Point Depression with Experimental Empirical Data

Figure 9.1 depicts the characteristic behavior of strong electrolytes. On the horizontal axis, the variable $\nu\gamma$, which measures the ion concentration, is plotted, and in which γ, as stated earlier, is the concentration of the electrolyte in moles per liter[1], while $\nu = \sum_i \nu_i$ represents the number of ions into which one molecule of the salt dissociates. Four representatives KCl, K_2SO_4, $La(NO_3)_3$ and $MgSO_4$ were selected from four types of salts distinguished by their ionic valences. KCl dissociates into two univalent ions, K_2SO_4 into one univalent and two bivalent ions, $La(NO_3)_3$ into three univalent and one trivalent ions, and $MgSO_4$ into two divalent ions. If we designate the freezing-point depression with Δ_k that is expected in the case of complete dissociation according to the classical theory, and the actual observed freezing-point depression with Δ, the expression is

$$\Theta = \frac{\Delta_k - \Delta}{\Delta_k}\,, \tag{9.1}$$

i.e. on the ordinate there is plottet the percentage deviation determined from the classical value. Following chapter 7 we also can set

$$\Theta = 1 - f_0\,. \tag{9.1'}$$

Θ, represented in this way, indicates the deviation of the osmotic coefficient from its limiting value 1. Because, in an aqueous solution,

$$\Delta_k = \nu \cdot \gamma \cdot 1.860^\circ \tag{9.2}$$

holds good, one point on the abscissa corresponds to a concentration for all electrolytes that should always produce the same freezing point-depression disregarding the mutual forces. We have plotted the observed values alone without the corresponding curve to avoid any interference. This method, however, was only made

[1]For the salts K_2SO_4, $La(NO_3)_3$, $MgSO_4$, instead of γ, the concentration γ' is used in moles per 1000 g of water, as given by the authors cited below, because, in the absence of measurements of the density of these salt solutions at 273 K, a conversion into moles per liter was not executable; this means only an insignificant deviation among the low concentrations considered here.

possible by the fact that some American researchers have recently carried out excellent measurements of freezing-point depression at low concentrations. The measurements of Figure 9.1 are from ADAMS and HALL and HARKINS, [1, 22].

It is evident that the deviation Θ does not increase, as the law of mass action would implicate, for small concentrations proportional to the first or even a higher power of the concentration.

Additionally, the curves demonstrate the strong influence of ion valence.

Our theory now requires that, at very low concentrations, the percentage deviation Θ should be proportional to the square root of the concentration, with a factor of proportionality that depends substantially on the valence of the ions. According to Equation 7.4 and Equation 7.5 (if the molecule dissociates into $\nu_1, \dots \nu_i, \dots \nu_s$ ions with valences $z_1, \dots z_i, \dots z_s$) it follows that

$$\Theta = 1 - f_0 = w \cdot \frac{e_0^2}{6\varepsilon k_\mathrm{B} T} \cdot \sqrt{\frac{4\pi e_0^2}{6\varepsilon k_\mathrm{B} T} \cdot n \cdot \sum_i \nu_i} \tag{9.3}$$

with the valence factor

$$w = \left(\frac{\sum_i \nu_i z_i^2}{\sum_i \nu_i} \right)^{\frac{3}{2}} . \tag{9.4}$$

It should now be expressed the number of ions n per cm^3 in the concentration γ, measured in moles per liter. We assume the value 6.06×10^{23} for AVOGADRO's constant, then

$$n = 6.06 \cdot 10^{20} \cdot \gamma \, .$$

Further, it is assumed that $e_0 = 4.77 \times 10^{-10}$ electrostatic units, $k_\mathrm{B} = 1.346 \times 10^{-16}\,\mathrm{erg\,Grad^{-1}}$, and, because the following deals with freezing-points of aqueous solutions, $T = 273$. For the dielectric constant of water, we take the formula of interpolation calculated by DRUDE from his measurements, according to which, [12], for 0 °C

$$\varepsilon = 88.23$$

results. Using these values (setting $\sum_i \nu_i = \nu$), the following holds good:

$$\sqrt{\frac{4\pi e_0^2}{\varepsilon k_\mathrm{B} T} \cdot n\nu} = 0.231 \cdot 10^8 \cdot \sqrt{\nu\gamma} \ \frac{1}{\mathrm{cm}}$$

and with this

$$\Theta = 0.270 \cdot w \cdot \sqrt{\nu\gamma} \, . \tag{9.5}$$

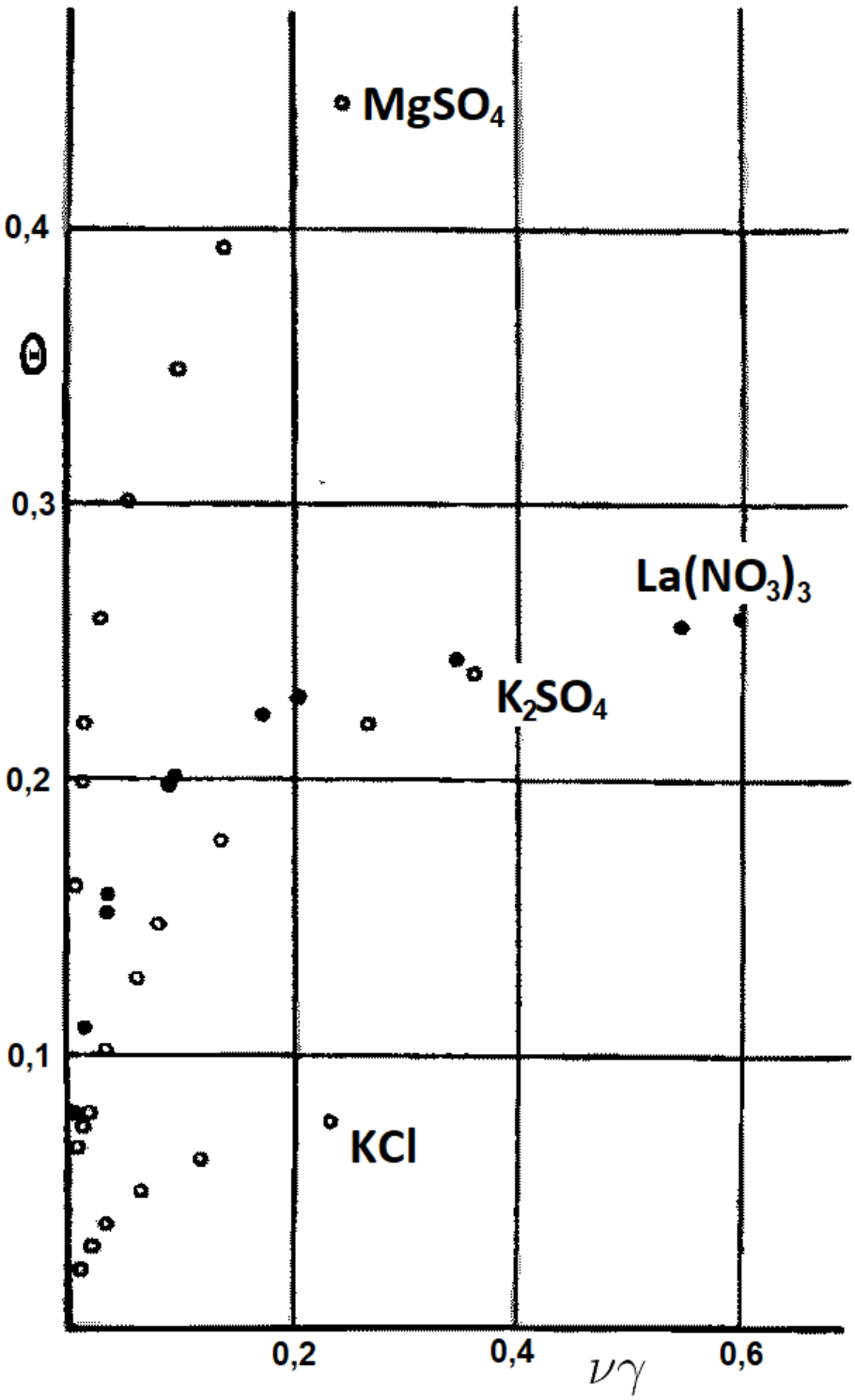

Figure 9.1.: The deviation of the osmotic coefficient Θ in dependence of the ion concentration $\nu\gamma$

The quantity $\varkappa$ becomes, using the above numerical values,

$$\varkappa = 0.231 \cdot 10^8 \cdot \sqrt{\nu\gamma} \cdot \sqrt{\frac{\sum_i \nu_i z_i^2}{\nu}} \; \frac{1}{\text{cm}} \,. \tag{9.6}$$

In Figure 9.2, observed values[2] of Θ were in contrast to the above plotted against the abscissa $\sqrt{\nu\gamma}$, i.e. the square root of $\nu\gamma$, and the observed points have been connected by straight lines.

Additionally, in the figure, four straight lines (red) originating from the coordinate origin are depicted, which represent the limiting law of Equation 9.5. The four types of salt in the figure have the valence factors

$$w = 1\,, \quad w = 2\sqrt{2}\,, \quad w = 3\sqrt{3}\,, \quad w = 8\,,$$

corresponding to the aforementioned straight lines. One can see that the approximation to the straight lines actually occurs for small concentrations, so that the limiting law with the square root of the concentration obviously corresponds to the facts. The absolute values of the slope (as expressed by the factor $0.270 \cdot w$ in Equation 9.5) calculated using the dielectric constant 88.23, and otherwise theoretically distinguished only by the valence factor, are confirmed by the experiment. However, Figure 9.2 shows that deviations from the limiting law start an early stage. This agrees with the considerations of chapter 3 and Equation 9.6, according to which, even in the case of uni-univalent electrolytes with $\gamma = 1$, the characteristic length $\frac{1}{\varkappa}$ is on the order of magnitude of the ion diameter, and that therefore it is no longer permissible to neglect the aforementioned. We have further based our theory on the simplified form of the potential equation according to Equation 4.1'. This too could have an effect. However, we pointed out (see page 18, footnote) that this latter effect is theoretically pretty small. The experimental results also indicate that the deviation from the limiting law are caused by the *individual* properties of the ions. To show this, we present Figure 9.3.

In this figure only observation are entered for uni-univalent salts[3] as a function of $\sqrt{2\gamma}$ (because here $\nu = 2$). The straight yellow line represents the limiting law discussed above. All curves tend to this straight line for small concentrations. The deviations are very different in magnitude and remarkably, e.g. in the case of the chloride salts in the order Cs, K, Na, and Li. This is the same sequence that results when alkali ions are ordered by decreasing mobility, a sequence that contradicts with the assumed size of the ions and, more recently by Born, [10], was considered to be correlated with the relaxation time of water for electrical

[2] [1, 22, 4], Concentration in mol per liter at KCl, $CuSO_4$; a mole per 1000 g of water at KNO_3, $BaCl_2$, K_2SO_4, $La(NO_3)_3$.

[3] In addition to the references cited, measurements by H. Jahn, [29, 30]; E. W. Washburn and MacInnes, [61]; W. H. Harkins and W. A. Roberts, [24], concentration partly in moles per liter, partly in moles per 1000 g of water.

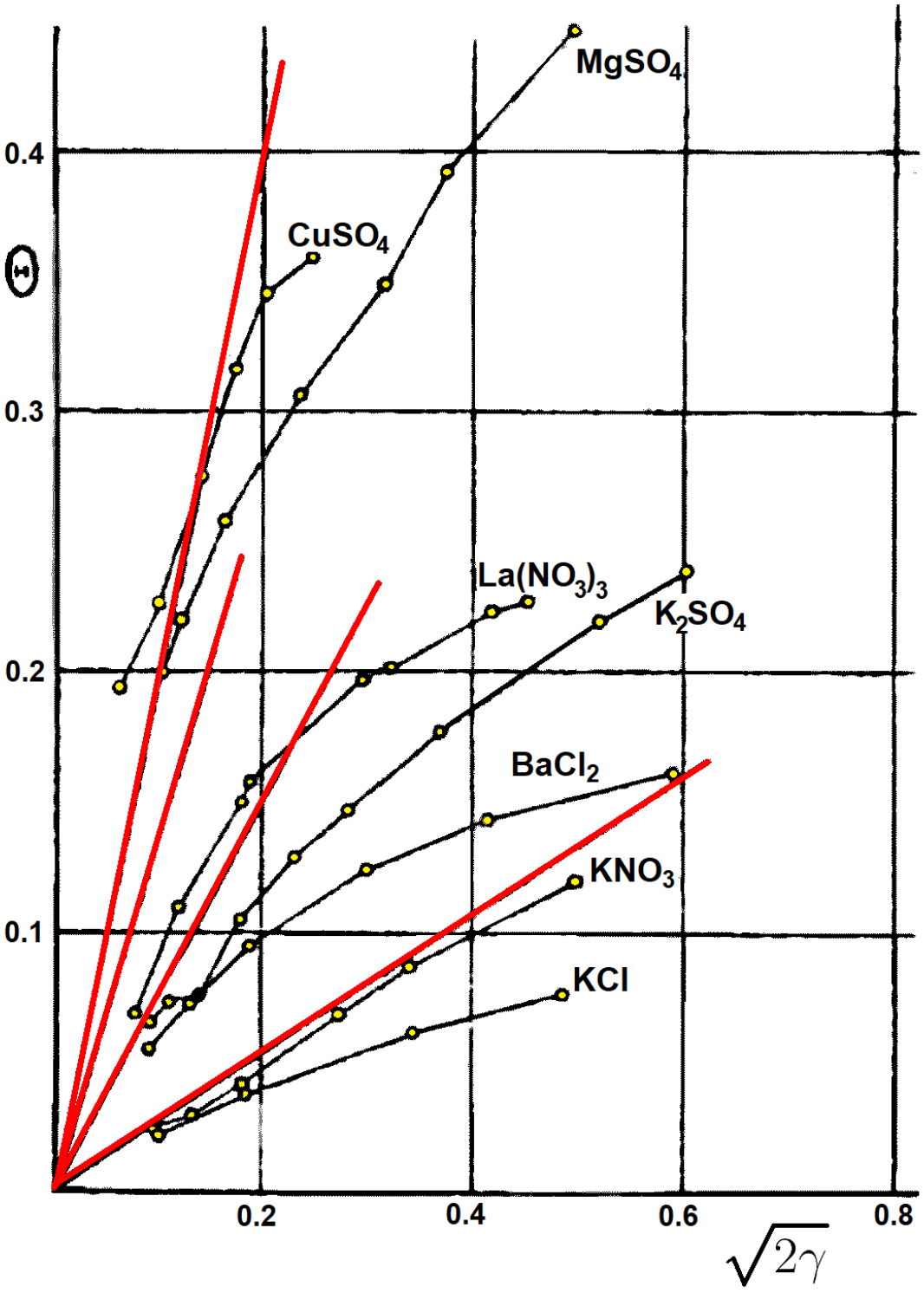

Figure 9.2.: The deviation of the osmotic coefficient Θ in dependence of the square root of the ion concentration $\sqrt{\nu\gamma}$. Straight lines representing the limiting law of Equation 9.5

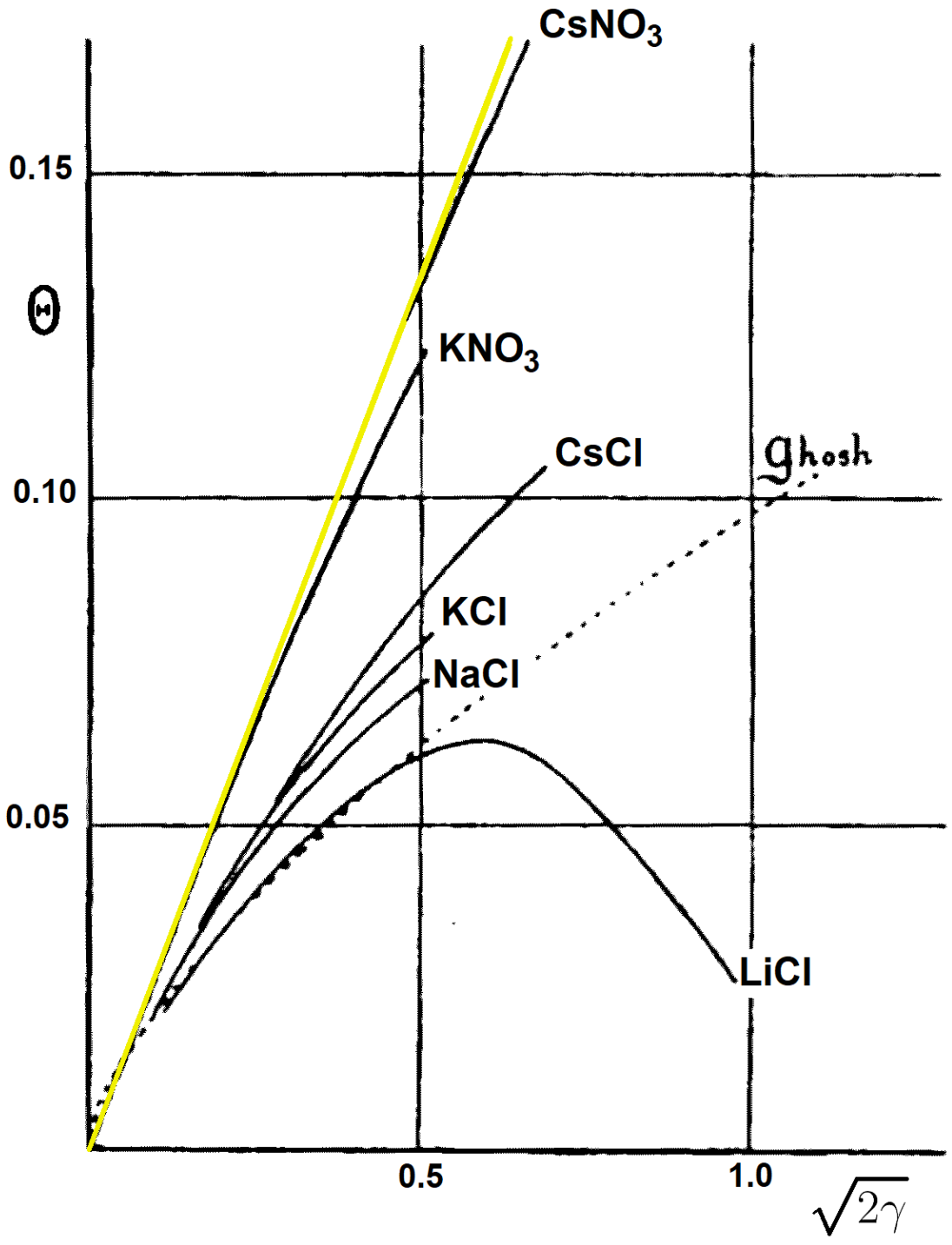

Figure 9.3.: The deviation of the osmotic coefficient Θ in dependence of the square root of the ion concentration $\sqrt{2\gamma}$ for uni-univalent salts. Straight yellow line representing the limiting law

polarization according to dipole theory. In order to allow an orientation towards the works by GHOSH, the curve for Θ is provided as a dashed line in the figure, as it results from that theory. It should simultaneously apply to all salts and also enters the origin with a vertical tangent.

The question then arises as to how far our theory, which has been improved by consideration of the ionic dimensions, is able to account for the individual deviations. The relationships shall be illustrated in Figure 9.4.

Again, we chose the four electrolytes from the four types mentioned above and plotted the observed values for Θ as a function of $\sqrt{\nu\gamma}$. According to Equation 7.6, considering the ionic size (after entering the numerical values), we have

$$\Theta = 1 - f_0 = 0.270 \cdot w \cdot \sqrt{\nu\gamma} \cdot \frac{\sum_i \nu_i z_i^2 \sigma_i}{\sum_i \nu_i z_i^2}\,, \tag{9.7}$$

In which σ_i means the function of the argument $x_i = \varkappa \cdot a_i$ tabulated on page 32 and represented by a formula in Equation 6.5, where a_i is the length which has to measure the size of the i-th ion relative to its surroundings. It seemed to us appropriate, in the present situation, not to investigate the individual sizes of ions, but to calculate with a mean diameter a that is the same for all ions of an electrolyte. Then all σ_i become equal to each other and one obtains for Θ the expression

$$\Theta = 0.270 \cdot w \cdot \sqrt{\nu\gamma} \cdot \sigma(\varkappa, a)\,. \tag{9.8}$$

For the determination of the magnitude of the value a, we chose only one, namely the point observed at the highest concentration, and then plotted the curve which results with this value a determined according to the theoretical Equation 9.8 in the figure. Four dashed straight lines extend from the origin (the tangents of the curves) representing the limiting law according to Equation 9.5 for large dilutions. The agreement with the observations is a very good one, especially in terms of the determination of the constant from a single observation point[4]. The figure is

[4]The method for determining a is explained in detail using the example of $La(NO_3)_3$. For $\gamma' = 0.17486$ there was observed $\Theta' = 0.2547$; because $\nu = 4$, the abscissa becomes $\sqrt{\nu\gamma'} = 0.836$. According to the limiting law Equation 9.5 for extreme dilution, with $w = 3\sqrt{3}$ (as it corresponds to $\nu_1 = 1$, ν_2, $z_1 = 3$, $z_2 = -1$ according to Equation 9.4) there would result $\Theta = 1.173$, the value actually observed is derived from this limit value by multiplication by 0.216. This factor is equal to σ according to Equation 9.8. From Figure 6.1 one now finds that to the ordinate $\sigma = 0.216$ there corresponds the abscissa $x = \kappa \cdot a = 1.67$; on the other hand, according to Equation 9.6, if $\sqrt{\nu\gamma'} = 0.836$ is inserted the value is $\varkappa = 0.336 \times 10^{-8}\,\mathrm{cm}^{-1}$. So the observed value correspond to the diameter

$$a = \frac{x}{\varkappa} = 4.97 \cdot 10^{-8}\ \mathrm{cm}\,.$$

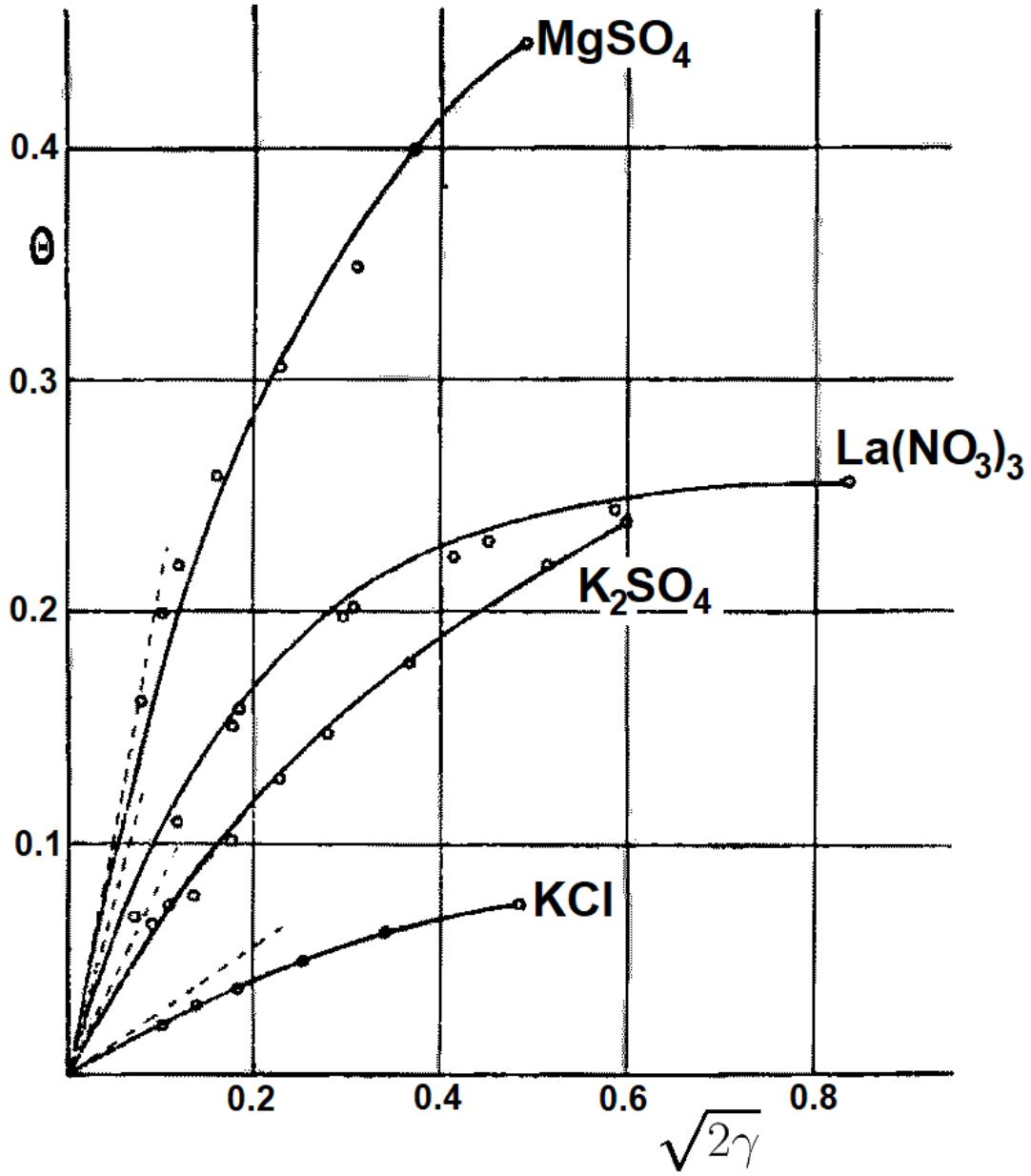

Figure 9.4.: Different plots of Θ against $\sqrt{2\gamma}$ to show validity of actual theory calculated according to Equation 9.8. Dashed straight lines show the limiting law according to Equation 9.5 for large dilutions

$2\gamma'$	$\sqrt{2\gamma'}$	Θ' observed	Θ' calculated
0.0100	0.100	0.0214	0.0237
0.0193	0.139	0.0295	0.0313
0.0331	0.182	0.0375	0.0392
0.0633	0.252	0.0485	0.0499
0.116	0.341	0.0613	0.0618
0.234	0.484	0.0758	–

Table 9.1.: KCl ($a = 3.76 \times 10^{-8}$ cm)

supplemented by the following tables:

In the first column, the respective ion concentration[5] $\nu\gamma$ is given, in the second column the abscissa $\sqrt{\nu\gamma}$ of Figure 9.4, in the third column the observed value of Θ[6] and in the fourth column the value of the same quantity calculated from Equation 9.8 and Equation 9.6. The number corresponding to the largest concentration is not given here, because it was used to calculate the value of the mean diameter a stated in the heading of the tables.

Finally, Figure 9.5 provides a plot of the theory and observation of aqueous KCl solutions. In discussing this figure, our primary goal is to make some remarks regarding the behavior of concentrated solutions; in addition, we intend to show how large the deviations are between the different results given in the literature by individual researchers with seemingly great accuracy. For this purpose, the figure contains all the observations we have found of KCl solutions since the year 1900, [2, 25, 31, 33, 5, 56, 63, 29, 30, 4, 15, 1, 57, 57].

As abscissa, $\sqrt{2\gamma}$ is chosen again, where γ is according to our definition the concentration in moles per liter of solution. All data referring to differently measured concentrations have been converted to those concentrations using measured densities, [3], of KCl solutions. The ordinate is again referred to as Θ but does not exactly

(For the salts K_2SO_4, $La(NO_3)_3$, $MgSO_4$, the concentration γ' is given in moles per 1000 g of water and was used instead of γ for the determination of Θ, which is therefore designated Θ'. For the low concentrations considered here, the deviations are very slight; a conversion from γ' to γ would not result in an appreciable change in the values for Θ' observed, Θ' calculated, and a.)

[5] see the previous note.

[6] see the previous note.

$3\gamma'$	$\sqrt{3\gamma'}$	Θ' observed	Θ' calculated
0.007 32	0.0906	0.0647	0.0612
0.0121	0.110	0.0729	0.0724
0.0185	0.136	0.0776	0.0871
0.0312	0.176	0.101	0.108
0.0527	0.229	0.128	0.132
0.0782	0.280	0.147	0.152
0.136	0.369	0.178	0.183
0.267	0.516	0.220	0.217
0.361	0.600	0.238	–

Table 9.2.: K_2SO_4 ($a = 2.69 \times 10^{-8}$ cm)

$4\gamma'$	$\sqrt{4\gamma'}$	Θ' observed	Θ' calculated
0.007 32	0.0906	0.0647	0.0612
0.0121	0.110	0.0729	0.0724
0.0185	0.136	0.0776	0.0871
0.0312	0.176	0.101	0.108
0.0527	0.229	0.128	0.132
0.0782	0.280	0.147	0.152
0.136	0.369	0.178	0.183
0.267	0.516	0.220	0.217
0.361	0.600	0.238	–

Table 9.3.: $La(NO_3)_3$ ($a = 4.97 \times 10^{-8}$ cm)

$2\gamma'$	$\sqrt{2\gamma'}$	Θ' observed	Θ' calculated
0.0064	0.0800	0.160	0.147
0.0107	0.103	0.199	0.179
0.0149	0.122	0.220	0.203
0.0262	0.162	0.258	0.248
0.0534	0.231	0.306	0.311
0.0976	0.312	0.349	0.368
0.138	0.372	0.392	0.400
0.242	0.493	0.445	–

Table 9.4.: $MgSO_4$ ($a = 3.35 \times 10^{-8}$ cm)

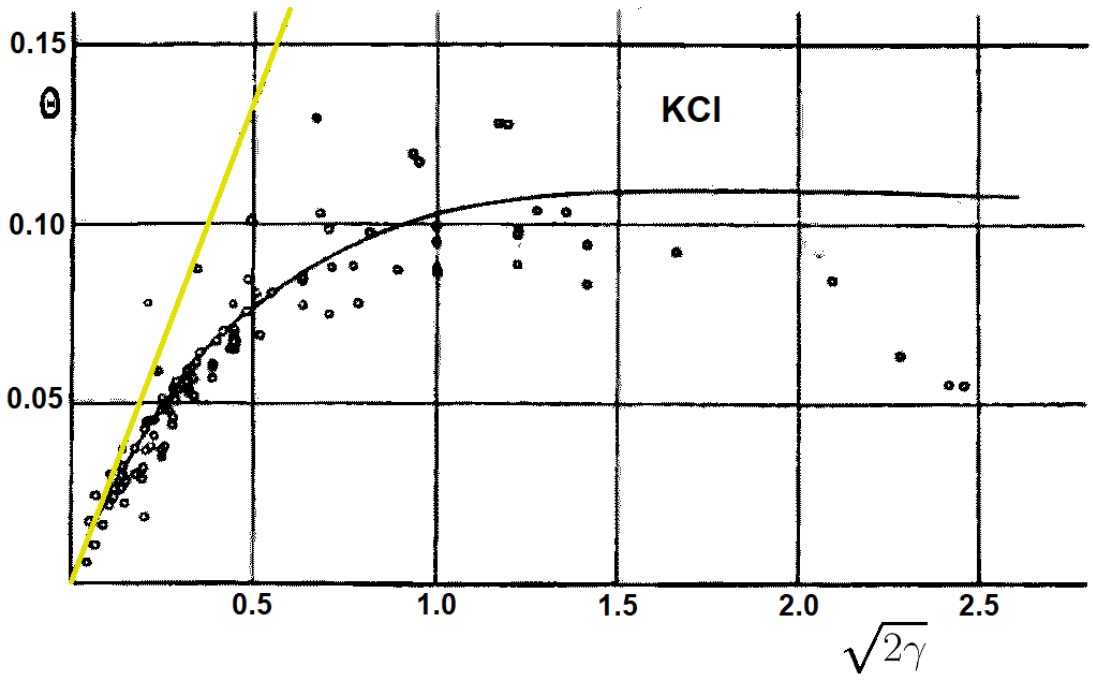

Figure 9.5.: Depiction of theory and observations in the case of KCl solutions, taking into account all relevant empirical data back to the year 1900. Straight yellow line representing the limiting law for extreme dilution corresponding to $\sigma = 1$

represent the previous expression

$$\frac{\Delta_k - \Delta}{\Delta_k} .$$

In fact, the classical theory, when it comes to concentrated solutions, no longer shows proportionality between freezing-point depression and concentration. The first reason for this is that $\log(1-c)$ appears in the classical equation, not the concentration c itself. Secondly, the difference between the thermodynamic potentials of ice and water is no longer accurately represented by the first term of the Taylor series, which is proportional to Δ; also the second term with Δ^2 must be retained. Accordingly, in this case, we have to use the whole of Equation 6.6. In the case of KCl, $n_1 = n_2 = n$ and $z_1 = -z_2 = 1$ are to be set, and also we wish to replace the two ion diameters a_1 and a_2 by a mean value a. Then Equation 6.6 can be arranged as follows:

$$\begin{aligned} &\frac{1}{2nv_0} \cdot \left\{ \frac{\Delta}{T_0} \cdot \frac{Q}{\mathscr{R}\, T_0} - \frac{\Delta}{T_0^2} \cdot \left[\frac{C_p - C'_p}{2\,\mathscr{R}} - \frac{Q}{\mathscr{R}\, T_0} \right] + \log(1-2c) \right\} \\ &= -\frac{e_0^2 \varkappa}{6\varepsilon k_\mathrm{B} T} \cdot \sigma \,. \end{aligned} \tag{9.9}$$

The left-hand term is now calculated for different concentrations. For this, we set $C_p - C'_p = 3.6$, corresponding to an approximate value for $C'_p = 14.4$, as extrapolated from Nernst's measurements, [52], of the specific heat of ice at 273 K. For the calculation it is further necessary to know the relationship between the molar concentration c and the volume concentration γ. With the aid of the observed density of the solution, this relation can be readily established; however, both here and in the derivation of the equation itself, the molecular weight of the water has a certain influence. As a first approximation, this influence vanishes, but the second-order members are not free from this influence. Insofar as this effect only plays a role to the second order, its influence is greatly diminished and this is why we have consistently used the simple molecular weight 18. The quantity $2nv_0$ in the denominator can finally be set equal to

$$2nv_0 = 2\Omega_0 \cdot \frac{\gamma}{1000} ,$$

if Ω_0 signifies the molar volume of water. If no mutual electrical effect of the ions were present, the left-hand term would have to be zero by inserting the observed freezing-point depression. In fact, it gives a finite value, and we call that value $-\Theta$. Then, according to the theory, this difference Θ must be represented by the right-hand side term, such that

$$\Theta = \frac{e_0^2 \varkappa}{6\varepsilon k_\mathrm{B} T} \cdot \sigma(\varkappa, a) = 0.270 \cdot \sqrt{2\gamma} \cdot \sigma(\varkappa, a) \tag{9.10}$$

should hold. Moreover, one will confirm that the definition of Θ obeyed here agrees with the limit given above for low concentrations.

The points, which are plotted in the figure, have the ordinates calculated from the observations using the outlined method. The curve in the figure represents the right-hand term of Equation 9.10, assuming $a = 3.76 \times 10^{-8}\,\mathrm{cm}$. This value of a was determined from an observation by Adams, according to which the experimental value $\Theta = 0.0758$ pertains to $\gamma = 0.117$. The straight yellow line, which is also plotted in the figure, again represents the limiting law for extreme dilution corresponding to $\sigma = 1$. It can be claimed that up $1\,\mathrm{mol\,L^{-1}}$ these observations are represented. At higher concentrations, the observations show a maximum for Θ. Although the theoretical curve has a maximum, this is, as the figure shows, so flat that it is hardly indicated. We would like to consider this difference to be real at large concentrations and comment on this in the next section.

10. General Remarks

It may be concluded from the preceding sections that it is inadmissible from the theoretical as well as the experimental viewpoint to consider the electrical energy of an ionic solution essentially determined by the mean mutual distance of the ions. Rather, a characteristic length proved to be a quantity that measures the thickness of the ionic cloud, or, to refer to a more familiar concept, the thickness of a HELMHOLTZ double-layer. Because this thickness depends on the concentration of the electrolyte, the electrical energy of the solution also becomes a function of this quantity. The limiting laws for large dilutions owe their characteristic nature, which is adapted to the power of $1/2$, to the fact that this thickness is inversely proportional to the square root of the concentration. We must therefore refrain from discussing a lattice structure of the electrolyte in the popular sense, and, as the development of the subject has shown, despite that it will lead to impermissible errors if one takes this image too literally, still a kernel of truth is contained in it. To make this clear, we will perform the following two thought experiments. First, take a unit of volume and think of moving it many times in succession to any points in the electrolyte. It is obvious that, in a binary electrolyte, one will encounter equally often a positive as a negative charged ion. Second, however, take the same unit of volume and place it in the electrolyte many times in succession, but now not quite arbitrarily but always such that it, for example, is always distant by a definite space (of several Å) from a randomly selected positive charged ion. Now, one will no longer encounter both positive and negative charges with the same frequency but more frequently the negative ones. Because in the immediate vicinity of each ion the oppositely charged ions predominate in number, one can rightly see an analogy to the crystal structure of the NaCl-type, where every Na-ion is directly surrounded by 6 Cl-ions and every Cl-ion by 6 Na-ions. However, it is important to note that an essential characteristic of the electrolyte solution is that to a certain degree of this order the former is determined by the thermal equilibrium between attractive forces and thermally induced movement, while it is predetermined in the crystal.

The calculations and the comparison with empirical knowledge were carried out in such a way that for the surrounding solvent the calculations were done using its usual dielectric constant. The success proves the validity of this assumption, but in itself this procedure is justified at low concentrations and should lead to errors at large concentrations. In fact, it follows from dipole theory that dielectrics at

high field strengths[1] must exhibit saturation phenomena that are similar to the known magnetic saturation. The recent experiments by Herweg, [27, 28], can be regarded as an experimental confirmation of this theoretical requirement. Because a field strength of approximately $200\,000\,\mathrm{V\,cm^{-1}}$ can be expected at a distance of $1 \times 10^{-7}\,\mathrm{cm}$ from a simply charged ion, one may exspect to observe some of these saturation phenomena. It would, of course, be very interesting if it were possible to extract that effect from these observations, even more that in this case nature offers us field strengths of a magnitude that would otherwise be difficult to attain by ordinary experimental means.

But also in other ways more concentrated solutions must exhibit special behavior. If there are many ions in the surroundings of each individual, this in turn may be considered a change of the surrounding medium in electrical terms, an effect that has not been considered in the preceding theory. In whatever way it may be effective, may emerge from the following consideration. Take an ion that is held captive and one that is mobile, possibly oppositely charged, and investigate the work required to remove the mobile ion. This work can then be regarded as consisting of two parts: firstly, the ion will consume some work to be removed, but secondly, one will gain work through subsequently filling the space previously occupied by the ion with the solvent. Now, experiments on the heat of dilution actually provide an indication of the real existence of such conditions. If, for example, a solution of HNO_3 of initially low concentration is used and it is diluted with a large amount of water (i.e., so much that further dilution would no longer produce a thermal effect), then cooling takes place, i.e., work must be done in the sense of the prior considerations to further separate the ions from each other. However, if the initial solvent has a larger concentration, heat will be generated in the same experiment, i.e., work is gained when in the surrounding of each ion enough other ions are removed and if these are replaced by water molecules. In conventional terms, this means that hydration of the ions predominantly occurs, and this process is considered to be an exothermic process. Obviously, the above considerations aim to interpret this so-called hydration with purely electrical methods. In fact, it is possible to make an approximate calculation that theoretically results in Berthelot's rules for the dependence of the heat of dilution on the initial concentration, and their practically found numerical coefficients make the same understandable in terms of order of magnitude. For the freezing-point observations, these considerations are meaningful in that they suggest the possibility of calculating why and to what extent the curves found for the percentage deviation Θ (see the case of KCl) bend downwards at higher concentrations and even cross the abscissa, provided the concentration is high enough. In this case, the freezing-point depression is greater than that which is to be expected classically (and also, explicitly stated, if the classical theory

[1] Field strength is the magnitude of a vector-valued field (e.g., in volts per meter, $\mathrm{V\,m^{-1}}$, for an electric field $\mathbf{E}$).

is used in its unabridged form). Until then, one had been contented to speak of hydration in such instances.

However, before the conditions for concentrated solutions can be investigated, it must first be shown that the irreversible process of conduction of the current in dilute strong electrolytes can be quantitatively tackled from the standpoint taken here. We reserve the detailed statements on this subject for the following article, see Part II, in which one will find their mathematical execution. Here we content ourselves with a presentation of the basic ideas. If an ion in the liquid moves under the influence of an external field strength, the surrounding ions must constantly rearrange in order to be able to form an ionic cloud. If one now assumes a charge has suddenly come into existence in the interior of the electrolyte, then the ionic cloud requires a certain relaxation time for its formation. Similarly, for a moving ion, the surrounding cloud will not be able to gain its equilibrium distribution, i.e. it will not be calculable on the basis of the BOLTZMANN-MAXWELL principle. However, its determination can be properly carried out with the equations for BROWNian motion. It can already be qualitatively estimated in what sense this effect can have be effective based on the presence of a finite relaxation time. At a point in front of the moving ion (i.e., a point toward which it moves), the electrical density of the ionic cloud must increase with time; for a point behind the ion, it must decrease. Owing to the effect of the relaxation time, however, the density before the ion will be somewhat smaller than its equilibrium value, but in the back it will not have dropped to its equilibrium value. As a result, during movement there is always a slightly larger electrical density of the cloud behind the ion than in front of the ion. Because charge density and ion charge always exhibit opposite signs, a force appears that slows the ion in its motion, regardless of its sign, and that obviously must increase with increasing concentration.

This is one effect that works in the same sense as the decrease of the degree of dissociation, which is otherwise calculated on the basis of OSTWALD's law of dilution. But there is a second effect that must also be considered. In the vicinity of one ion there exist predominantly ions of opposite sign, which, of course, move in the opposite direction under the influence of an external field. These ions will drag with them the surrounding solvent to some extent. This means, therefore, that the individual ion considered does not have to move relative to a stationary solvent but rather relative to a solvent moving in the opposite direction. Because, apparently, this effect increases with increasing concentration, one has a second effect, which acts in the same sense as a decrease of the degree of dissociation. The effect can be calculated quantitatively using the same principles that HELMHOLTZ used to treat electrophoresis[2].

[2]Each ion, travelling through the solution, will experience a frictional effect owing to the viscosity

The commonality of the two influences mentioned is, as the calculation shows, that both are directly related to the thickness of the ionic cloud and therefore the forces generated are proportional to the square root of the concentration of the electrolyte, at least in the limit for very low concentrations. This results in a law discovered many years ago based on KOHLRAUSCH's observational material, [43], according to which, at low concentrations, the percentage deviation of the molecular conductivity from its limit value is proportional to the square root of the concentration with infinitesimal dilution. Of course, the proportionality factor also has its molecular significance in this way.

Anticipating the detailed presentation of the conditions of electrolytic conduction in the following article, we can conclude as a result of the whole account that the notion, according to which the strong electrolytes are completely dissociated, is entirely supported.

Zurich, February 1923.
(Received February 27, 1923.)

of the liquid. However, this frictional effect itself depends on concentration, since, with increasing concentration, encounters between the solvent sheaths of oppositely charged ions will become more frequent. The solvent molecules in the solvation sheaths are moving with the ions, and therefore an individual ion will experience an additional drag associated with the solvent molecules in the solvation sheaths of oppositely charged ions; this is termed the *electrophoretic effect*, [23].

Part II.

The theory of electrolytes. II. The Limiting Law for Electrical Conductivity

1. Introduction

It was already noted in the introduction to our first note on electrolytes (see Part I) that the conductivity curve (see Figure 1.1 and Figure 1.2), viewed as a function of concentration, cannot be explained using the law of mass action. As we want to maintain in the following, one introduces a "conductivity coefficient" f_λ, defined similarly to the earlier osmotic coefficient f_0, namely such that

$$\Lambda_\mathrm{m} = f_\lambda \cdot \Lambda_\mathrm{m}^0$$

when Λ_m means about the molecular conductivity (molar conductivity) at any concentration and Λ_m^0 means the same size in the limit for vanishing concentration (limiting molar conductivity).

If, for example, one has a binary electrolyte of concentration c, and one assumes that the known reduction in molecular conductivity with increasing concentration is a consequence of a relative reduction in the number of ions following the law of mass action, one can calculate that for small concentrations the following should hold:

$$1 - f_\lambda = \frac{c}{K}$$

K then means the equilibrium constant that is decisive for the suggested equilibrium between ions and molecules. Experience with strong electrolytes contradicts this conclusion. The curves that represent A as a function of concentration, and several of which are drawn, for example, in the well-known book by Kohlrausch and Holborn, show a very special curvature at small concentrations, and it is not we are talking about the fact that, as the law of mass action requires, they lead linearly to their limit value for zero concentration. Rather, they reach it with a vertical tangent. Kohlrausch tried to establish a law that would approximate the course of the curve over a larger range. He found approach, [40, 34],

$$1 - f_\lambda \sim \sqrt[3]{c}$$

suitable. One usually finds this approach cited. Kohlrausch himself noticed that it only holds the value of an interpolation formula and fails both at large and, what is particularly more important, at small concentrations. Here he finds the other approach, [41, 35],

$$1 - f_\lambda \sim \sqrt{c}$$

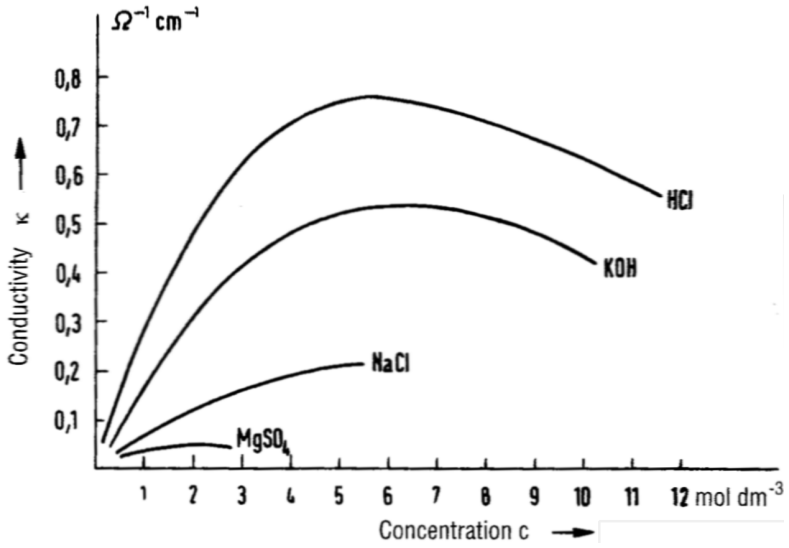

Figure 1.1.: Conductivity of aqueous electrolyte solutions as a function of concentration at 18 °C, taken from [23]

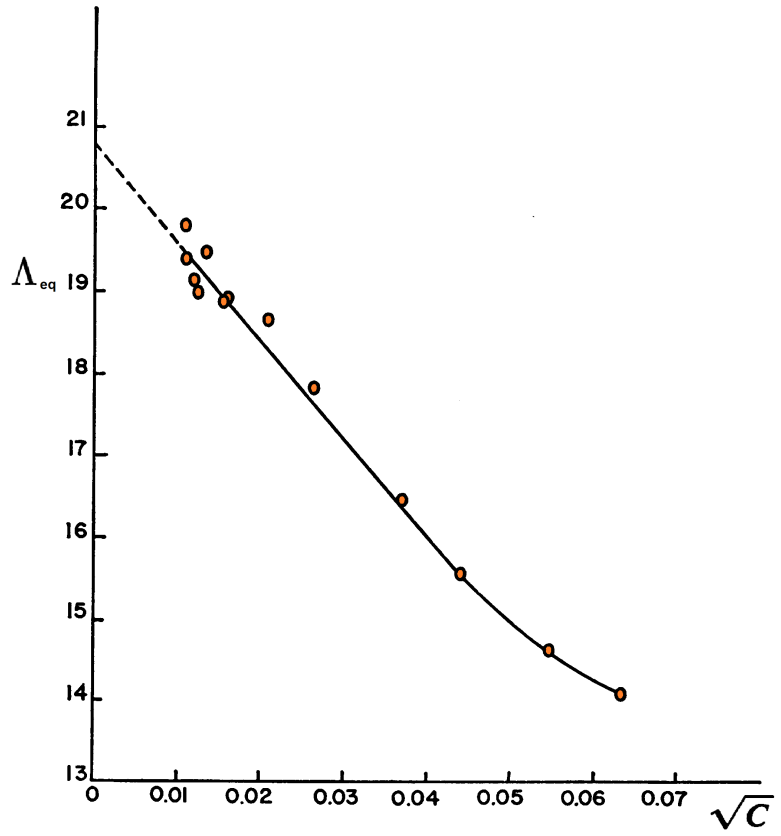

Figure 1.2.: KOHLRAUSCH plot of equivalent conductance Λ_{eq}, against $\sqrt{C}$ for KCI solutions in water saturated 1-butanol, taken from [48]

much more suitable. In view of the fact that very little attention is paid to this fact, that the law with the power 1/2 has even occasionally been completely forgotten and from the interpolation formula with the power 1/3 theoretical conclusions are drawn, we would like to quote the words with which KOHLRAUSCH accompanies the establishment of the limiting law with the 1/2 power. They are, [41, 35]:

"If the course of conduction changes with such sharpness into such a simple characteristic with increasing dilution, then I consider it very likely that this characteristic represents the law. Of course, this does not correspond to the wish that it can be derived from the theory of dissociation."

The following attempts to calculate how the mutual electrical forces of the ions will influence the conductivity, assuming complete dissociation. At the end of our first note we have already made the qualitative considerations, which should be carried out quantitatively here. It may be permissible to briefly formulate the two reasons given there for the reduction in molecular conductivity when the concentration increases. In pure solvent, an ion moves under the sole influence of the external field strength and reaches such a velocity that the friction force it experiences is equal to the external force acting on it. If the solution now reaches a certain concentration, then, firstly, an additional force will arise in addition to the external force, which increases with increasing concentration and is caused by the mutual COULOMB forces of the ions. Secondly, the friction force that the ion experiences will also change due to the presence of the other ions. Both causes have the effect of reducing conductivity. The magnitude of the effects that are attempted to be calculated in chapter 2 and chapter 3 is linked to the mean thickness of the ionic cloud. This itself was inversely proportional to the square root of the concentration at small concentrations. So one understands that the square root will play a role, and the theory actually provides KOHLRAUSCH's law

$$1 - f_\lambda \sim \sqrt{c}\,.$$

Since the limiting case of small concentrations gives rise to many considerations, we have consistently limited ourselves to this case in the following and have not tried to expand the formulæ so that they could also be applied to larger concentrations.

In chapter 4 the considerations are then combined into a formula for the conductivity coefficient. Finally, theory and experience are compared in chapter 5.

As also stated in our first note, there are two calculations with the same end goal; one from P. HERTZ, [26], the second from J. Ch. GHOSH, [16, 17, 18, 19, 20, 20]. Even if we are of the opinion that P. HERTZ's calculation probably goes too far in

its idealization, which is practically expressed in the fact that it does not explain KOHLRAUSCH's limiting law, so it is but of particular value as a consistent attempt to record the mutual hindrance of the ions. We have the impression that J. Ch. GHOSH's later work on the subject is less important. It also leaves KOHLRAUSCH's law unexplained. Furthermore, in contrast to HERTZ, the effect of mutual hindrance is not discussed at all. The only approach is that as the concentration increases, a certain proportion of the ions of the completely dissociated electrolyte can no longer be viewed as free. This part is calculated supposedly using BOLTZMANN's principle. We do not believe that this principle has been used here in the sense intended.

2. Ionic Forces

2.1. Fundamental Equation to Determine the Distribution Function

An ion is moved in the x direction with the constant linear velocity v. The ionic cloud that forms around this ion can no longer be calculated according to the BOLTZMANN-MAXWELL principle because there is no longer a static case, and we have to resort a little further to a conditional equation, which can also determine the distribution function now. This is accomplished by the completed and suitably interpreted equation for the BROWNian motion, as used by P. DEBYE in a similar way, for example, to calculate the anomalous dipole dispersion.

Let there be a distribution of particles with the instantaneous distribution function f in a space with the space element $\mathrm{d}S$. The number of particles $f \cdot \mathrm{d}S$ present in the space element $\mathrm{d}S$ will then change for two reasons.

During a small observation time τ the particles will disperse according to a certain probability function w as a result of their thermal motion. As a result, the element $\mathrm{d}S$ loses all its particles $f \cdot \mathrm{d}S$ except for an amount of smaller magnitude; but it gains the number of particles

$$f' \cdot \mathrm{d}S' \cdot w \cdot \mathrm{d}S\,.$$

from each element $\mathrm{d}S'$. The total increase in the number of particles in the time τ as a result of the thermal movement is therefore, for which the probability function w is formed:

$$-f \cdot \mathrm{d}S + \mathrm{d}S \cdot \int f' \cdot w \,\mathrm{d}S'\,.$$

If τ is chosen to be sufficiently small so that only the immediate vicinity of $\mathrm{d}S$ is taken into account, then

$$\begin{aligned} f' = f &+ \left(x \cdot \frac{\partial f}{\partial x} + \cdots + \cdots \right) \\ &+ \frac{1}{2} \cdot \left(x^2 \cdot \frac{\partial^2 f}{\partial x^2} + \cdots + \cdots + 2xy \cdot \frac{\partial^2 f}{\partial x\, \partial y} + \cdots \right) \end{aligned}$$

can be set according to TAYLOR's theorem and only the mean values

$$\begin{aligned}
\overline{x} &= \int x \cdot w \, \mathrm{d}S' \,, \\
&\vdots \\
\overline{x^2} &= \int x^2 \cdot w \, \mathrm{d}S' \,, \\
&\vdots \\
\overline{xy} &= \int xy \cdot w \, \mathrm{d}S' \\
&\vdots
\end{aligned}$$

are to be determined. Now, the following holds:

$$\begin{aligned}
\overline{x} = \overline{y} = \overline{z} = 0 \,, \\
\overline{xy} = \overline{yz} = \overline{zx} = 0 \,, \\
\overline{x^2} = \overline{y^2} = \overline{z^2} = \overline{s^2} \,,
\end{aligned}$$

where s^2 remains tentatively undetermined. Thus, the increase in the number of particles sought for is due to the thermal movement

$$\frac{s^2}{2} \cdot \left(\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \right) \mathrm{d}S = \frac{s^2}{2} \cdot \operatorname{div} \operatorname{grad} f \cdot \mathrm{d}S \,.$$

A second cause for the change in the number of particles can be found in the effect of existing forces. Assume that a force $\mathfrak{K}$ acting on a particle produces a velocity $\mathfrak{v}$, according to the equation

$$\mathfrak{K} = \xi \cdot \mathfrak{v} \,,$$

so that ξ represents the friction constant associated with the particle. Then it follows in a known manner for the increase in the number of particles brought about by the effect of $\mathfrak{K}$

$$-\tau \cdot \operatorname{div} f \cdot \frac{\mathfrak{K}}{\xi} \cdot \mathrm{d}S \,.$$

A third cause of the change in the number of particles will be the movement of the liquid in which the particles are suspended. However, this influence is not taken into account in the approximation, which we do not want to go beyond here. Accordingly, the total increase in the number of particles is

$$\tau \cdot \frac{\partial f}{\partial t} \cdot \mathrm{d}S = \frac{s^2}{2} \cdot \operatorname{div} \operatorname{grad} f \cdot \mathrm{d}S - \tau \cdot \operatorname{div} \frac{f \mathfrak{K}}{\xi} \cdot \mathrm{d}S \,,$$

i.e. the distribution function is to be determined as a function of time and position according to the equation

$$\tau \cdot \frac{\partial f}{\partial t} = \operatorname{div}\left(\frac{s^2}{2} \cdot \operatorname{grad} f - f \cdot \frac{\mathfrak{K}}{\xi} \cdot \tau\right) .$$

From the fact that the solution of this equation in the static case must correspond to the Boltzmann-Maxwell principle, one now concludes in the well-known way since Einstein

$$\frac{s^2}{2\tau} = \frac{k_\mathrm{B} T}{\xi} .$$

The basic equation then takes the form

$$\varrho \cdot \frac{\partial f}{\partial t} = \operatorname{div}\left(k_\mathrm{B} T \operatorname{grad} f - f \cdot \mathfrak{K}\right) . \tag{2.1}$$

2.2. Generell Conditions to Determine the Ionic Cloud

Ions of different types

$$1, \ldots i, \ldots s ,$$

may be present in the solution with the charges

$$q_1, \ldots q_i, \ldots q_s .$$

A specific ion is picked out and forced to move in the x direction with velocity v. The ion numbers

$$n_1 \,\mathrm{d}S \ldots n_i \,\mathrm{d}S \ldots n_s \,\mathrm{d}S$$

will then be found on average in a space element $\mathrm{d}S$.

A current flows through the solution, created under the influence of a constant electric field strength $\mathscr{E}$, which should also be directed in the x direction. Firstly, a force

$$\mathfrak{K}' = c_i \cdot \mathscr{E}$$

acts on an ion of the i-th type.

Similar to the previous static case, a distribution of ions will develop around the highlighted ion, so that at least the oppositely charged ones will predominate in the vicinity. The cloud formed in this way will, on average, give rise to an electrical potential ψ, and if we calculate with this average potential ψ for reasons similar to those in the static case, then a second force on an ion of the type i exists of magnitude

$$-q_i \cdot \operatorname{grad} \psi .$$

Using the basic Equation 2.1, we can now use the equation to determine the particle number n_i

$$\xi_i \cdot \frac{\partial n_i}{\partial t} = \mathrm{Div}\left(k_\mathrm{B}T \cdot \mathrm{Grad}\, n_i - n_i q_i \mathscr{E} + n_i q_i \cdot \mathrm{Grad}\, \psi\right) . \tag{2.2}$$

Here ξ_i is the friction constant for particles of type i; In addition, we wrote Div and Grad instead of div and grad because from now on we want to distinguish between a space-fixed coordinate system that is denoted by capital case letters, and another moving coordinate system, denoted by lower case letters, which is supposed to move with the highlighted ion. There are as many equations of Equation 2.2 as there are types of ions; they would be sufficient to determine the n_i, i.e. the desired ion distribution, if the unknown potential did not occur. Now ψ must satisfy the Poisson equation. We can therefore make the system complete by adding this equation

$$\mathrm{Div}\,\mathrm{Grad}\,\psi = -\frac{4\pi}{\varepsilon} \cdot \sum_i n_i q_i \,. \tag{2.2'}$$

Here ε means the dielectric constant of the solvent.

It is clear from the start that the particle numbers n_i as well as the potential ψ will be stationary with respect to a coordinate system that moves with the highlighted ion. So if we set

$$\begin{aligned} X - v \cdot t &= x \,, \\ Y &= y \,, \\ Z &= z \,, \end{aligned}$$

then the quantities we are looking for depend only on x, y, z. Accordingly the following holds:

$$\begin{aligned} \frac{\partial}{\partial t} &= -v \cdot \frac{\partial}{\partial x} \,, \\ \mathrm{Div} &= \mathrm{div} \,, \\ \mathrm{Grad} &= \mathrm{grad} \,, \end{aligned}$$

and we get the system:

$$\left.\begin{aligned} &\vdots \\ -\xi_i v \cdot \frac{\partial n_i}{\partial x} &= \mathrm{div}\left(k_\mathrm{B}T \cdot \mathrm{grad}\, n_i - n_i q_i \mathscr{E} + n_i q_i \,\mathrm{grad}\, \psi\right) \\ &\vdots \\ \mathrm{div}\,\mathrm{grad}\,\psi &= -\frac{4\pi}{\varepsilon} \cdot \sum_i n_i q_i \,. \end{aligned}\right\} \tag{2.3}$$

2.3. Approximations and Their Physical Meaning

If one were to set the velocity $v = 0$ in Equation 2.3 and also let $\mathscr{E}$ vanish, one would have the possibility of satisfying the first s equations using the approach

$$n_i = \text{const.} \cdot e^{-\frac{q_i \psi}{k_\mathrm{B} T}} ;$$

because they would then take the form:

$$\operatorname{div} (k_\mathrm{B} T \cdot \operatorname{grad} n_i + n_i q_i \cdot \operatorname{grad} \psi) = 0 . \tag{2.4}$$

This would then, as corresponds to our earlier statements, be the Boltzmann-Maxwell approach. However, we did not use this entire approach before, but used a power series expansion of the exponential functions and only considered the first term of the expansion. This procedure can be justified independently using Equation 2.4 as follows. At a greater distance from the highlighted ion, n_i will tend to a constant value $\overline{n_i}$, which can be identified with the average density of the i-th kind of ions in the liquid. If $\operatorname{grad} \psi$ is sufficiently small, and this will be all the more true the more diluted the solution is, then instead of

$$n_i q_i \cdot \operatorname{grad} \psi$$

the following can be written:

$$\overline{n_i} q_i \cdot \operatorname{grad} \psi$$

Hence Equation 2.4 becomes

$$\operatorname{div} (k_\mathrm{B} T \cdot \operatorname{grad} n_i + \overline{n_i} q_i \cdot \operatorname{grad} \psi) = 0$$

and can be satisfied by the Ansatz

$$n_i = \overline{n_i} - \frac{\overline{n_i} q_i}{k_\mathrm{B} T} \cdot \psi . \tag{2.5}$$

But this is nothing other than the beginning of the expansion of the Maxwell-Boltzmann approach, which was the basis for all statements in the static case. We therefore remain within this framework if from now on we insert in the first s equations of Equation 2.3 instead of

$$-n_i q_i \mathscr{E} + n_i q_i \operatorname{grad} \psi$$

the following equation:

$$-\overline{n_i} q_i \mathscr{E} + \overline{n_i} q_i \operatorname{grad} \psi .$$

The "external" field strength is justifiably assumed to be at most of the same order of magnitude with $\operatorname{grad} \psi$. However, the modified Equation 2.3 for the moving

ion are still not fulfilled by the approach according to Equation 2.5, because a deviation of the MAXWELL-BOLTZMANN distribution must be caused through the movement. We therefore make the Ansatz:

$$n_i = \overline{n_i} - \frac{\overline{n_i} q_i}{k_\mathrm{B} T} \cdot \psi + \mu_i \tag{2.6}$$

where μ_i measures the deviation from the equilibrium distribution. It will not be necessary to consider terms which are of higher than first order in v. But since μ_i vanishes with v, terms of the form $v \cdot \mu_i$, for example, can be safely neglected. If all these conditions are taken into account, then one can transit from Equation 2.3 to the following system with practically sufficient precision:

$$\left.\begin{aligned} &= \vdots \\ \xi_i v \cdot \frac{\overline{n_i} q_i}{k_\mathrm{B} T} \cdot \frac{\partial \psi}{\partial x} &= \operatorname{div}\left(k_\mathrm{B} T \cdot \operatorname{grad} \mu_i\right) = k_\mathrm{B} T \cdot \operatorname{div} \operatorname{grad} \mu_i \\ &= \vdots \\ \operatorname{div} \operatorname{grad} \psi &= \frac{4\pi}{\varepsilon k_\mathrm{B} T} \cdot \sum_i \overline{n_i} q_i^2 \psi - \frac{4\pi}{\varepsilon} \cdot \sum_i \mu_i q_i \,, \end{aligned}\right\} \tag{2.7}$$

if one bears in mind that

$$\operatorname{div} \mathscr{E} = 0 \quad \text{and} \quad \sum_i \overline{n_i} q_i = 0 \,.$$

The quantity

$$\frac{4\pi}{\varepsilon k_\mathrm{B} T} \cdot \sum_i \overline{n_i} q_i^2$$

already appeared in the static case. We denoted it $\varkappa^2$, which shall be done here too. It is the square of the reciprocal length, which in turn measures the thickness of the ionic cloud. If we now apply the operation

$$\Delta = \operatorname{div} \operatorname{grad}$$

to the last equation of Equation 2.7, then the first s equations can immediately be used to eliminate the μ_i and we get

$$\Delta\left(\Delta\psi - \varkappa^2 \psi\right) = -\frac{4\pi}{\varepsilon k_\mathrm{B} T} \cdot \frac{v}{k_\mathrm{B} T} \cdot \sum_i \overline{n_i} q_i^2 \xi_i \cdot \frac{\partial \psi}{\partial x} \,.$$

We now introduce an average friction constant ξ using the approach

$$\xi = \frac{\sum_i \overline{n_i} q_i^2 \xi_i}{\sum_i \overline{n_i} q_i^2} \,, \tag{2.8}$$

and further denote the quantity $\frac{\xi v}{k_\mathrm{B} T}$, which is proportional to the velocity, by

$$\frac{\xi v}{k_\mathrm{B} T} = \omega \,. \tag{2.9}$$

With these abbreviations the potential equation results in:

$$\Delta \left(\Delta \psi - \varkappa^2 \psi \right) = -\varkappa^2 \omega \cdot \frac{\partial \psi}{\partial x} \,; \tag{2.10}$$

within this, both $\varkappa$ and ω are quantities of the dimension of a reciprocal length. The only issue now is to find a solution to Equation 2.10 that satisfies the conditions of the problem.

2.4. The Potential Distribution Around a Moving Ion

The potential does not need to be determined exactly using Equation 2.10. It is sufficient to work out the solution up to the first order in v, i.e. in ω. So we will use the well-known procedure of first setting the right term equal to 0 and determining ψ in the zeroth approximation. We will then enter this value for ψ on the right and then calculate ψ as a first approximation based on this equation.

As zeroth approximation the potential

$$A \cdot \frac{e^{-\varkappa \cdot r}}{r}$$

of the static case comes of course into consideration, although we do not yet enter the value of the constant A, and r means the distance from the highlighted ion. Thus, the potential for the moving ion is determined with sufficient precision by the equation

$$\Delta \left(\Delta \psi - \varkappa^2 \psi \right) = -\varkappa^2 \omega \cdot \frac{\partial}{\partial x} \left(A \cdot \frac{e^{-\varkappa \cdot r}}{r} \right) \,. \tag{2.10'}$$

Now note that according to the definition

$$\Delta \left(A' \cdot \frac{e^{-\varkappa \cdot r}}{r} \right) = \varkappa^2 \cdot \left(A \cdot \frac{e^{-\varkappa \cdot r}}{r} \right) \,.$$

A special solution of Equation 2.10' is obtained from the equation

$$\begin{aligned}\Delta\psi - \varkappa^2\psi &= -\omega \cdot \frac{\partial}{\partial x}\left(A \cdot \frac{e^{-\varkappa \cdot r}}{r}\right) \\ &= -\omega \cdot \frac{\mathrm{d}}{\mathrm{d}r}\left(A \cdot \frac{e^{-\varkappa \cdot r}}{r}\right) \cdot \cos(\vartheta)\,,\end{aligned}$$

if the angle between x and r is denoted by ϑ. Since furthermore, if

$$\psi = R \cdot \cos(\vartheta)$$

is set, the following relation holds:

$$\Delta\psi - \varkappa^2\psi = \left(\frac{1}{r^2} \cdot \frac{\mathrm{d}}{\mathrm{d}r}r^2 \cdot \frac{\mathrm{d}R}{\mathrm{d}r} - \frac{2R}{r^2} - \varkappa^2 R\right) \cdot \cos(\vartheta)\,,$$

then it is easy to convince oneself that

$$R = -\frac{\omega A}{2} \cdot e^{-\varkappa \cdot r}\,.$$

The special solution corresponding to the right term is therefore

$$\psi = -\frac{\omega A}{2} \cdot e^{-\varkappa \cdot r} \cdot \cos(\vartheta)\,. \tag{2.11}$$

However, an approach can be added to this solution that satisfies the equation:

$$\Delta\left(\Delta\psi - \varkappa^2\psi\right) = 0\,.$$

We also set this part proportional to $\cos(\vartheta)$ and get

$$\psi = \left(A' \cdot \frac{\mathrm{d}}{\mathrm{d}r}\frac{e^{-\varkappa \cdot r}}{r} + A'' \cdot \frac{\mathrm{d}}{\mathrm{d}r}\frac{e^{\varkappa \cdot r}}{r} + \frac{B'}{r^2} + B'' \cdot r\right) \cdot \cos(\vartheta)\,. \tag{2.11'}$$

In this expression, however, those terms that do not vanish at infinity obviously are not allowed to be retained. Therefore we have to set:

$$A'' = 0 \quad \text{and} \quad B'' = 0$$

This ultimately results in using Equation 2.11 and Equation 2.11':

$$\begin{aligned}\psi = A \cdot \frac{e^{-\varkappa \cdot r}}{r} + \Bigg(&-\frac{\omega A}{2} \cdot e^{-\varkappa \cdot r} \\ &+A' \cdot \frac{\mathrm{d}}{\mathrm{d}r}\frac{e^{-\varkappa \cdot r}}{r} + \frac{B'}{r^2}\Bigg) \cdot \cos(\vartheta)\,.\end{aligned} \tag{2.12}$$

The determination of the constants now follows. If one examines the additional potential caused by the movement near the zero point and expands to powers of r for this purpose, the result is

$$\left[(-A' + B') \cdot \frac{1}{r^2} + \frac{-\omega A + \varkappa^2 A'}{2} + \left(\frac{\omega A}{2} - \frac{\varkappa^2 A'}{3}\right) \cdot \varkappa r + \cdots\right] \cdot \cos(\vartheta)\,.$$

We want to consider the dimensions of the highlighted ion to be negligibly small compared to $\frac{1}{\varkappa}$. This goes hand in hand with the fact that, as emphasized in the introduction, we limit ourselves to the limiting laws for large dilution. The first term in the square brackets must then vanish so that

$$B' = A'\,, \tag{2.13}$$

otherwise the highlighted ion would appear at the zero point to be a carrier of a fixed dipole, whose potential is proportional to $\frac{\cos(\vartheta)}{r^2}$ is. But the second term must also vanish, so that

$$\varkappa^2 A' = \omega A\,. \tag{2.14}$$

If one calculates

$$\operatorname{div}\operatorname{grad} = \Delta$$

of the additional potential, that term would result in an value that is proportional to $\frac{\cos(\vartheta)}{r^2}$; However, according to Poisson's equation, this would mean that the density of the electricity distribution corresponding to the additional potential in the vicinity of the highlighted ion would be infinitely large. Since this is not permissible, Equation 2.14 is also justified. If the charge of the highlighted ion is q_j, then the constant A has a value of

$$A = \frac{q_j}{\varepsilon}\,, \tag{2.15}$$

and in summary we get

$$\psi = \frac{q_j}{\varepsilon} \cdot \frac{e^{-\varkappa \cdot r}}{r} - \omega \cdot \frac{q_j}{\varepsilon} \cdot \left(\frac{e^{-\varkappa \cdot r}}{2} - \frac{\mathrm{d}}{\mathrm{d}(\varkappa \cdot r)} \frac{e^{-\varkappa \cdot r}}{\varkappa \cdot r} - \frac{1}{\varkappa^2 \cdot r^2}\right) \cdot \cos(\vartheta)\,. \tag{2.16}$$

for the potential of the moving ion.

2.5. Field and Charge Distribution Around a Moving Ion

With the help of POISSON's equation, the mean electrical density of the ionic cloud is obtained from the value given in Equation 2.16 for the potential. One can find the expression

$$-\frac{q_j \varkappa^3}{4\pi} \cdot \frac{e^{-\varkappa \cdot r}}{\varkappa \cdot r} + \frac{\omega}{2} \cdot \frac{q_j \varkappa^2}{4\pi} \cdot e^{-\varkappa \cdot r} \cdot \cos(\vartheta) \,.$$

for this.

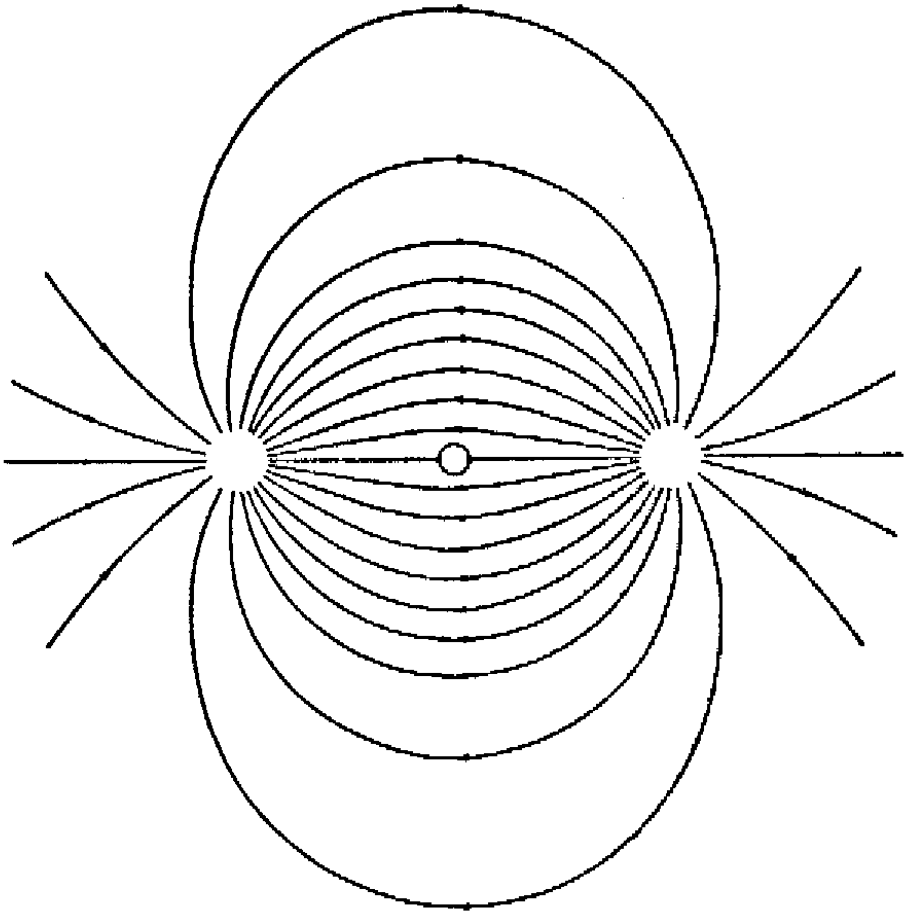

Figure 2.1.: Lines of force around a moving ion

The first term corresponds to the static case ($\omega = 0$) and gives a centrically symmetrical density distribution with a sign that is consistently opposite to the ion charge q_j. The second term, on the other hand, results in the change that occurs as a result of the movement. In front of the ion ($\vartheta = 0$), the charge density is the same as that of the highlighted ion; behind the ion ($\vartheta = \pi$) it has the opposite

sign. So one can already see here, in accordance with the qualitative considerations in our first note, that forces must arise that have a frictional effect. To give an idea, a line of force image is shown in Figure 2.1, which shows the lines of force as they are caused by the additional part of the potential created as a result of the movement. One can see how that additional field becomes isotropic near the zero point, where the ion is located and assumed to have the charge q_j. This is confirmed and at the same time the value of the additional field strength prevailing there is found by expanding the additional potential according to powers of r. For the total potential ψ it follows therefore:

$$\psi = \frac{q_j}{\varepsilon} \cdot \frac{e^{-\varkappa \cdot r}}{r} + \frac{\omega \varkappa}{6} \cdot \frac{q_j}{\varepsilon} \cdot r \cdot \cos(\vartheta) + \cdots . \tag{2.17}$$

So in the vicinity of the zero point the additional potential is equal to

$$\frac{\omega \varkappa}{6} \cdot \frac{q_j}{\varepsilon} \cdot r \cdot \cos(\vartheta) = \frac{\omega \varkappa}{6} \cdot \frac{q_j^2}{\varepsilon} \cdot \varkappa$$

of a field strength corresponding to a value of

$$\mathscr{E} = -\frac{\omega \varkappa}{6} \cdot \frac{q_j}{\varepsilon} .$$

The force that occurs as a result of the finite relaxation time of the ionic cloud is therefore

$$q_j \cdot \mathscr{E} = -\frac{\omega \varkappa}{6} \cdot \frac{q_j^2}{\varepsilon} . \tag{2.18}$$

Firstly, it is always frictional (because of the negative sign) regardless of the sign of q_j. Secondly, it is proportional to the velocity v of the moving ion, because ω is, according to Equation 2.9, an abbreviation for the expression

$$\omega = \frac{\xi v}{k_\mathrm{B} T} .$$

As a result, it acts like an ordinary friction force. The mean friction constant appearing in the definition of ω is defined by

$$\xi = \frac{\sum_i \overline{n_i} q_i^2 \xi_i}{\sum_i \overline{n_i} q_i^2} ;$$

according to Equation 2.8. For example, if there are easily mobile ions (ξ_i small), then ξ is also small and the additional friction force becomes small. This corresponds to the expectation, because easily mobile ions will need a shorter time to form the ionic cloud. The deviations from the static potential distribution will therefore be smaller. Finally, the dielectric constant ε in the denominator of Equation 2.18 measures in a known manner the reduction in the force effect between the charges

that occurs in the electrical medium. The additional Figure 2.2 serves to illustrate the lines of force of the entire field. In the static case, the lines of force would spread out radially and in a straight line from the ion. The movement causes them to experience a curvature, as if they can only follow the ion's movement with a certain delay.

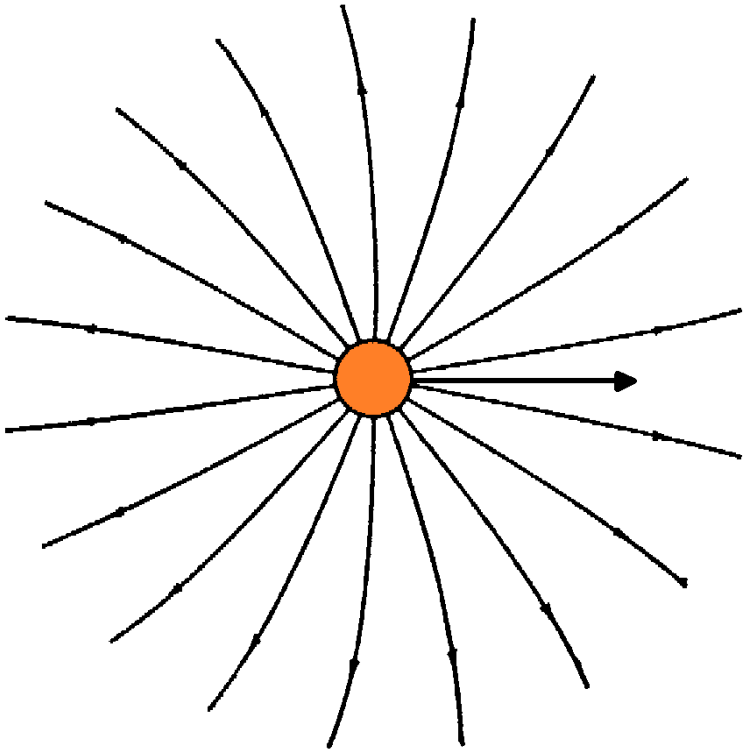

Figure 2.2.: Demonstration of the total electric field with its distorted lines of force spreading from the center of a moving ion

In order to get an idea of the magnitude of the additional friction force caused by the movement, all ξ_i are assumed to be equal to one another. Then the usual frictional force that the ion would experience in pure water is $\xi \cdot v$. Thus, the ratio of the additional force according to Equation 2.18 to this original friction force will be

$$\frac{q_j^2 \varkappa}{6\varepsilon k_\mathrm{B} T}\,.$$

Assume a monovalent ion such that $q_j = e_0 = 4.77 \times 10^{-10}\,\mathrm{statC}$ and set (at $0\,^\circ\mathrm{C}$)

$\varepsilon = 88.23$, $T = 273\,\mathrm{K}$ and $k_\mathrm{B} = 1.346 \times 10^{-16}\,\mathrm{erg\,Grad^{-1}}$, it follows for the ratio[1]

$$\frac{q_j^2 \varkappa}{6\varepsilon k_\mathrm{B} T} = 1.17 \cdot 10^{-8} \cdot \varkappa\,.$$

For a solution of a uni-univalent salt with the concentration γ in moles per liter, we previously found the reciprocal length[2]

$$\varkappa = 0.326 \cdot 10^8 \cdot \sqrt{\gamma}\ \ \mathrm{cm^{-1}}\,;$$

In this case it would be therefore

$$\frac{q_j^2 \varkappa}{6\varepsilon k_\mathrm{B} T} = 0.382 \cdot \sqrt{\gamma}\,.$$

It can therefore be seen that the additional forces arising as a result of the finite relaxation time become significant compared to the usual forces of ionic friction even at relatively small concentrations.

[1] If exact (actual) values are used, the older value only differs marginally from the new one. $\frac{\left(4.8032047 \cdot 10^{-10}\right)^2}{6 \cdot 87.9 \cdot 273.15 \cdot 1.380649 \cdot 10^{-16}} = 1.16 \cdot 10^{-8}$, $\Delta = 1.008$.

[2] $\frac{1}{\varkappa}$ corresponds, for example, at a concentration $\gamma = 2\,\mathrm{mol\,L^{-1}}$ to a length of 68.6 Å.

3. Electrophoretic Forces

3.1. Equations of Motion for the Solvent

As is well known, it is possible, with a certain degree of approximation, to calculate the frictional forces that the ions experience during their transport as if they were small spheres moving in a rubbing liquid and thereby generating flows according to the macroscopic laws of the hydrodynamics of fluid friction. From the fluid movement calculated in this way, the well-known STOKES's law follows, according to which the friction force that occurs is equal to

$$6\pi\eta b v\,,$$

if η means the coefficient of friction and b means the radius of the moving sphere. We want to build on the image of the moving sphere to determine whether and how the flow of the liquid will change if ionic charges are present in it. What is of interest to us is less the absolute STOKES result than the changes that will have to be made to it as a result of the presence of the ions. Given the small size of the ions, one can of course be very doubtful as to whether the calculation based on the basic equations of hydrodynamics is still applicable. However, it seems to us that this doubt should not be given too much weight, although it is clear from the outset that the radii that have to be introduced will only correspond in magnitude to the real dimensions of the ions. However, the applicability of the following calculation method to the mobility of colloid particles and their influence by added electrolytes would remain unaffected by such an objection.

The ion with charge q_j, viewed as a sphere of radius b, moves in the x direction of a coordinate system with velocity v. It will take its ionic cloud with it, in which the electricity is distributed on average with a certain density, which can be derived from a potential ψ. For this potential we make the Ansatz

$$\psi = \frac{q_j}{\varepsilon} \cdot \frac{e^{-\varkappa \cdot r}}{r}\,; \tag{3.1}$$

ψ is therefore the approach given earlier for the static case and in the limit for large dilution, which satisfies the equation

$$\Delta\psi - \varkappa^2\psi = 0\,. \tag{3.2}$$

The movement of the ion with the velocity v takes place under the influence of the electric field strength $\mathscr{E}$ that generates the current, which should only have a component in the x direction, namely $\mathscr{E}_x = X$. The difference compared to the STOKES case is based on the fact that there is now an electrical charge corresponding to the ionic cloud in every volume element of the liquid, so that the external field strength $\mathscr{E}$ generates a force acting on the volume that will change the flow pattern. Since the charge in the cloud is opposite to the ion, it immediately follows that the flow will change in such a way that friction is increased. According to POISSON's equation, the density of electricity is

$$-\frac{\varepsilon}{4\pi} \cdot \Delta\psi \,,$$

so the force acting on the volume has the value

$$\mathfrak{F} = -\frac{\varepsilon\,\mathscr{E}}{4\pi} \cdot \Delta\psi = -\frac{\varepsilon\,\mathscr{E}}{4\pi} \cdot \varkappa^2\psi \,. \tag{3.3}$$

In Part I it was discussed that the potential around the moving ion is no longer accurately represented by Equation 3.1. If we still calculate with Equation 3.1, this is done because, in the context of the introduction, we only consider the limiting case of very dilute solutions. For the same reason, it is possible to decompose the problem, as is done in chapter 2 and chapter 3. Strictly speaking, one would have to take the liquid flow (as already indicated in chapter 2) into account when determining the distribution function, and the still-to-be-determined distribution function or the potential when determining the liquid flow respectively. Accordingly, strictly speaking, the following equations form a system with the earlier ones, which must be treated as a whole. The decomposition into two separate systems is just a consequence of our limitation to small concentrations.

Now let the velocity of the fluid flow be $\mathfrak{v}$, then according to STOKES the hydrodynamic equations are:

$$\left.\begin{aligned} \eta \cdot \operatorname{rot}\operatorname{rot}\mathfrak{v} &= -\operatorname{grad} p + \mathfrak{F} \,, \\ \operatorname{div}\mathfrak{v} &= 0 \,, \end{aligned}\right\} \tag{3.4}$$

where $\mathfrak{F}$ is to be inserted according to Equation 3.3 and Equation 3.1 and p means the pressure.

Our goal is first to determine the velocity $\mathfrak{v}$ of the liquid as a function of position, and we want to solve the problem assuming that the ion sphere is at rest and the liquid has a velocity $-v$ at a large distance in the x direction. The real case can then be obtained simply by superimposing a constant velocity $+v$ in the x

direction, whereby the flow does not change relative to the ion sphere. After the velocity distribution is known, the stresses on the surface of the sphere are then calculated and the force that the ion experiences is determined from these stresses.

One notices that the whole problem is set up in a very similar way to how H. v. Helmholtz had already solved it, when he calculated the phenomena of electrophoresis. The only difference is that we determine the constitution of the ionic cloud, which corresponds to the Helmholtz double layer, in terms of thickness and electricity distribution using the potential ψ.

3.2. General Form of the Distribution of Velocity and Pressure

If we first form the div of the first equation of Equation 3.4, it follows with respect to Equation 3.3 and with the assumption made regarding the direction of $\mathfrak{F}$

$$\Delta p = \operatorname{div} \mathfrak{F} = -\frac{\varepsilon X}{4\pi} \cdot \Delta \frac{\partial \psi}{\partial x} \,. \tag{3.5}$$

A special solution is

$$p = -\frac{\varepsilon X}{4\pi} \cdot \frac{\partial \psi}{\partial x} \,,$$

to which has to be added an arbitrary solution of the kind

$$\Delta p = 0 \,.$$

From now on we introduce spherical coordinates according to the adjacent Figure 3.1 and make the Ansatz:

$$\begin{aligned} p = &\left(A_0 + \frac{B_0}{r} \right) \\ &+ \left(A_1 \cdot r + \frac{B_1}{r^2} - \frac{\varepsilon X}{4\pi} \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r} \right) \cdot \cos(\vartheta) \,, \end{aligned} \tag{3.6}$$

in which A_0, B_0, A_1, B_1 represent arbitrary constants and

$$\frac{\partial \psi}{\partial x} = \frac{\mathrm{d}\psi}{\mathrm{d}r} \cdot \cos(\vartheta)$$

was set.

Now we form the rot of the first equation of Equation 3.4 and first focus on the

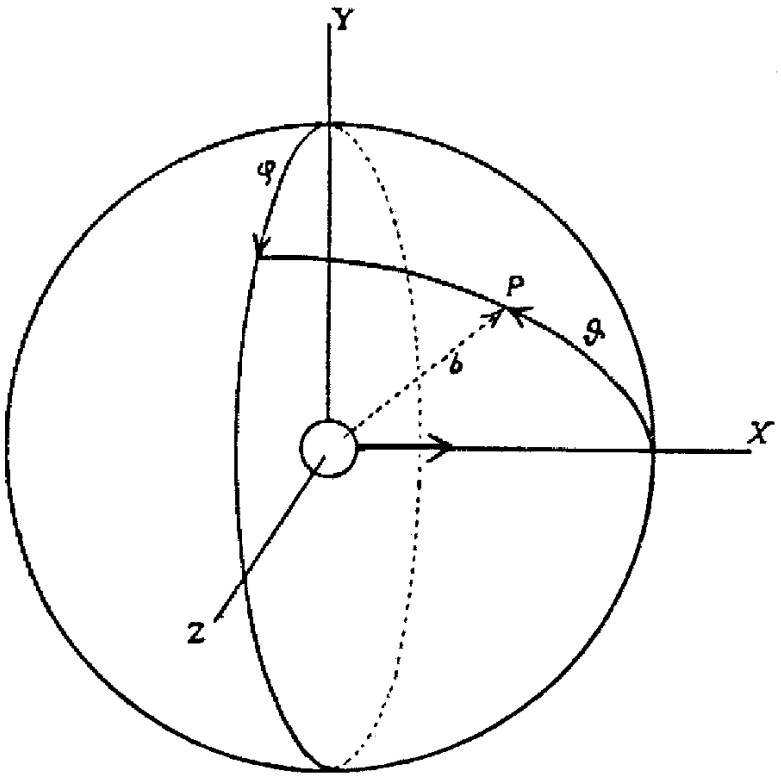

Figure 3.1.: Scheme of introducing spherical coordinates for making an *Ansatz* for Equation 3.6

strength of vorticity

$$\mathfrak{w} = \operatorname{rot} \mathfrak{v} \,. \tag{3.7}$$

To determine $\mathfrak{w}$ we get:

$$\eta \cdot \operatorname{rot} \operatorname{rot} \mathfrak{w} = \operatorname{rot} \mathfrak{F} \,. \tag{3.8}$$

According to the assumptions of the problem, the flow in every meridian plane passing through the x axis is the same. So $\mathfrak{v}_r$ and $\mathfrak{v}_\vartheta$ exist, while $\mathfrak{v}_\vartheta = 0$. However, since in general the three components of $\mathfrak{w}$ in the r, ϑ and φ directions are to be determined explicitly according to Equation 3.7 using the equations

$$\begin{aligned}
\mathfrak{w}_r &= \frac{1}{r \cdot \sin(\vartheta)} \cdot \frac{\partial}{\partial \vartheta} \sin(\vartheta) \mathfrak{v}_\varphi - \frac{1}{r \cdot \sin(\vartheta)} \cdot \frac{\partial}{\partial \varphi} \mathfrak{v}_\vartheta \,, \\
\mathfrak{w}_\vartheta &= \frac{1}{r \cdot \sin(\vartheta)} \cdot \frac{\partial}{\partial \varphi} \mathfrak{v}_r - \frac{1}{r} \cdot \frac{\partial}{\partial r} r \mathfrak{v}_\varphi \,, \\
\mathfrak{w}_\varphi &= \frac{1}{r} \cdot \frac{\partial}{\partial r} r \mathfrak{v}_\vartheta - \frac{1}{r} \cdot \frac{\partial}{\partial \vartheta} \mathfrak{v}_r \,,
\end{aligned}$$

so there is only one component of $\mathfrak{w}$ in the φ direction (the vortex lines form circles

around the x axis), i.e.

$$\begin{aligned}\mathfrak{w}_r &= 0\,,\\ \mathfrak{w}_\vartheta &= 0\,,\\ \mathfrak{w}_\varphi &= \mathfrak{w}_\varphi\,.\end{aligned}$$

Now the vector $\operatorname{rot}\operatorname{rot}\mathfrak{w}$ has to be formed from the vector $\mathfrak{w}$ and, as one can easily see, this again has only one φ component that results in

$$\begin{aligned}\left(\operatorname{rot}\operatorname{rot}\mathfrak{w}\right)_p = &-\frac{1}{r^2}\cdot\frac{\partial^2}{\partial r^2}r\mathfrak{w}_\varphi\\ &-\frac{1}{r^2}\cdot\frac{\partial}{\partial\vartheta}\cdot\frac{1}{\sin(\vartheta)}\cdot\frac{\partial}{\partial\vartheta}\sin(\vartheta)\mathfrak{w}_\varphi\,.\end{aligned}$$

Similarly, since $\mathfrak{F}$ is directed in the X direction, $\operatorname{rot}\mathfrak{F}$ also has only one φ component of magnitude

$$\operatorname{rot}_\varphi\mathfrak{F} = -\varkappa^2\cdot\frac{\varepsilon X}{4\pi}\cdot\sin(\vartheta)\cdot\frac{\mathrm{d}\psi}{\mathrm{d}r}\,.$$

The only existing φ component of the vortex strength $\mathfrak{w}$ must therefore satisfy the equation

$$\begin{aligned}&\frac{1}{r}\cdot\frac{\partial^2}{\partial r^2}r\mathfrak{w}_\varphi + \frac{1}{r^2}\cdot\frac{\partial}{\partial\psi}\frac{1}{\sin(\vartheta)}\cdot\frac{\partial}{\partial\vartheta}\sin(\vartheta)\mathfrak{w}_\varphi\\ &= -\varkappa^2\cdot\frac{\varepsilon X}{4\pi\eta}\cdot\sin(\vartheta)\cdot\frac{\mathrm{d}\psi}{\mathrm{d}r}\,.\end{aligned}\tag{3.9}$$

If now $\mathfrak{w}_\varphi$ is set proportionally to $\sin(\vartheta)$ and if one takes into account the differential equation that ψ satisfies, one easily gets the solution

$$\mathfrak{w}_\varphi = \left(C_1\cdot r + \frac{D_1}{r^2} - \frac{\varepsilon X}{4\pi\eta}\cdot\frac{\mathrm{d}\psi}{\mathrm{d}r}\right)\cdot\sin(\vartheta)\,,\tag{3.10}$$

where C_1 and D_1 are constants yet to be determined.

The two results according to Equation 3.6 for the pressure and Equation 3.10 for the vortex strength were obtained using the basic equations Equation 3.4 after they have been differentiated in a suitable way (by forming div and rot). Therefore, $\mathfrak{w}_\varphi$ and p must now be inserted into the undifferentiated basic equation to see whether the statements agree with each other, or what relationships between the constants A_1, B_1, A_1, B_1, C_1, D_1 must exist for this to be the case.

The equation

$$\begin{aligned}\eta \cdot \operatorname{rot}\operatorname{rot}\mathfrak{v} &= -\operatorname{grad} p + \mathfrak{F} \\ &= -\operatorname{grad} p - \frac{\varepsilon\,\mathscr{E}}{4\pi} \cdot \varkappa^2 \psi\end{aligned}$$

breaks down into three component equations for the r, the ϑ, and the φ directions. One notices that the third equation, relating to the φ direction, takes the form $0 = 0$, corresponding to the fact that $\mathscr{E}$ has only the components $\mathscr{E}_r$, and $\mathscr{E}_\vartheta$. The first two equations are:

$$\left.\begin{aligned}&\left(2\eta C_1 + 2\eta \cdot \frac{D_1}{r^3} - \frac{\varepsilon X}{4\pi} \cdot \frac{2}{r} \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r}\right) \cdot \cos(\vartheta) \\ &= \frac{B_0}{r^2} + \left(-A_1 + \frac{2B_1}{r^3} + \frac{\varepsilon X}{4\pi} \cdot \frac{\mathrm{d}^2\psi}{\mathrm{d}r^2}\right) \cdot \cos(\vartheta) \\ &- \frac{\varepsilon X}{4\pi} \cdot \varkappa^2 \psi \cdot \cos(\vartheta)\,, \\ &\left(-2\eta C_1 + \eta \cdot \frac{D_1}{r^3} + \frac{\varepsilon X}{4\pi} \cdot \frac{1}{r} \cdot \frac{\mathrm{d}}{\mathrm{d}r} r \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r}\right) \cdot \sin(\vartheta) \\ &= \left(A_1 + \frac{B_1}{r^3} - \frac{\varepsilon X}{4\pi} \cdot \frac{1}{r} \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r}\right) \cdot \sin(\vartheta) \\ &+ \frac{\varepsilon X}{4\pi} \cdot \varkappa^2 \psi \cdot \sin(\vartheta)\,.\end{aligned}\right\} \tag{3.11}$$

So one concludes from that

$$\begin{aligned}B_0 &= 0\,, \\ A_1 + 2\eta C_1 &= 0\,, \\ B_1 - \eta D_1 &= 0\,,\end{aligned}$$

or

$$\left.\begin{aligned}B_0 &= 0\,, \\ C_1 &= -\frac{A_1}{2\eta}\,, \\ D_1 &= \frac{B_1}{\eta}\,,\end{aligned}\right\} \tag{3.12}$$

while the terms associated with X actually cancel each other out with respect to the differential equation valid for ψ. In summary, we get according to Equation 3.6

and Equation 3.10 and using Equation 3.12

$$\left.\begin{aligned} p &= A_0 + \left(A_1 \cdot r + \frac{B_1}{r^2} - \frac{\varepsilon X}{4\pi} \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r}\right) \cdot \cos(\vartheta)\,, \\ \mathfrak{w}_r &= 0\,, \\ \mathfrak{w}_\vartheta &= 0\,, \\ \mathfrak{w}_\varphi &= \left(-\frac{A_1}{2\eta} \cdot r + \frac{B_1}{\eta} \cdot \frac{1}{r^2} - \frac{\varepsilon X}{4\pi\eta} \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r}\right) \cdot \sin(\vartheta)\,. \end{aligned}\right\} \tag{3.13}$$

It remains to draw conclusions from the expression obtained for the vortex strength $\mathfrak{w} = \operatorname{rot}\mathfrak{v}$ to the velocity $\mathfrak{v}$ itself, of course taking into account the incompressibility condition $\operatorname{div}\mathfrak{v} = 0$. The two equations under consideration are explicitly:

$$\left.\begin{aligned} \mathfrak{w}_\varphi = \operatorname{rot}_\varphi \mathfrak{v} &= \frac{1}{r} \cdot \frac{\partial}{\partial r} r\mathfrak{v}_\vartheta - \frac{1}{r} \cdot \frac{\partial}{\partial \vartheta}\mathfrak{v}_r \\ &= \left(-\frac{A_1}{2\eta} \cdot r + \frac{B_1}{\eta} \cdot \frac{1}{r^2} - \frac{\varepsilon X}{4\pi\eta} \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r}\right) \cdot \sin(\vartheta)\,, \\ \operatorname{div}\mathfrak{v} &= \frac{1}{r^2} \cdot \frac{\partial}{\partial r} r^2\mathfrak{v}_r + \frac{1}{r \cdot \sin(\vartheta)} \cdot \frac{\partial}{\partial \vartheta} \sin(\vartheta) \cdot \mathfrak{v}_\vartheta = 0\,. \end{aligned}\right\} \tag{3.14}$$

Now set

$$\left.\begin{aligned} \mathfrak{v}_r &= R_1 \cdot \cos(\vartheta)\,, \\ \mathfrak{v}_\vartheta &= R_2 \cdot \sin(\vartheta)\,, \end{aligned}\right\} \tag{3.15}$$

where R_1 and R_2 mean two yet-to-be-determined functions of r alone, then instead of Equation 3.14 we get

$$\left.\begin{aligned} \frac{1}{r} \cdot \frac{\mathrm{d}}{\mathrm{d}r} r R_2 + \frac{R_1}{r} &= -\frac{A_1}{2\eta} \cdot r + \frac{B_1}{\eta} \cdot \frac{1}{r^2} - \frac{\varepsilon X}{4\pi\eta} \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r}\,, \\ \frac{1}{r^2} \cdot \frac{\mathrm{d}}{\mathrm{d}r} r^2 R_1 + 2 \cdot \frac{R_2}{r} &= 0\,. \end{aligned}\right\} \tag{3.14'}$$

But by considering $r^2 \cdot R_1$ and $r \cdot R_2$ as required functions, one can also replace this system with the following:

$$\left.\begin{aligned} &\frac{\mathrm{d}^2}{\mathrm{d}r^2}\left(r^2 R_1\right) - \frac{2}{r^2} \cdot \left(r^2 R_1\right) \\ &= \frac{A_1}{\eta} \cdot r^2 - \frac{2B_1}{\eta} \cdot \frac{1}{r} + \frac{\varepsilon X}{2\pi\eta} \cdot r \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r}\,, \\ &= (rR_2) + \frac{1}{2} \cdot \frac{\mathrm{d}}{\mathrm{d}r}\left(r^2 R_1\right) = 0\,. \end{aligned}\right\} \tag{3.16}$$

The solution of the first equation of Equation 3.15 corresponding to the right term

has the form

$$r^2 R_1 = \frac{A_1}{\eta} \cdot \frac{r^4}{10} + \frac{B_1}{\eta} \cdot r + \frac{\varepsilon X}{2\pi\eta\varkappa^2} \cdot r \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r} \,.$$

The correctness of the latter term which is proportional to X follows easily with regard to the differential equation which is satisfied by ψ. A solution to the homogeneous equation can be added to this result, so that overall we get:

$$\begin{aligned} r^2 R_1 = {} & \frac{A_1}{\eta} \cdot \frac{r^4}{10} + \frac{B_1}{\eta} \cdot r + A_3 r^2 + B_3 \cdot \frac{1}{r} \\ & + \frac{\varepsilon X}{2\pi\eta\varkappa^2} \cdot r \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r} \,, \end{aligned}$$

introducing two new constants A_3 and B_3. The second equation of Equation 3.15 gives as an immediate result

$$\begin{aligned} r R_2 = {} & -\frac{A_1}{2\eta} \cdot \frac{2}{5} \cdot r^3 - \frac{B_1}{2\eta} - A_3 r \\ & + \frac{B_3}{2} \cdot \frac{1}{r^2} - \frac{\varepsilon X}{4\pi\eta\varkappa^2} \cdot \frac{\mathrm{d}}{\mathrm{d}r} r \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r} \,. \end{aligned}$$

If one now takes into account the formulation of the Ansatz according to Equation 3.15 and takes p from Equation 3.13, the following velocity and pressure distribution is finally obtained, which satisfies the hydrodynamic equations:

$$\left.\begin{aligned} \mathfrak{v}_r &= \left[\frac{A_1}{\eta} \cdot \frac{r^2}{10} + \frac{B_1}{\eta} \cdot \frac{1}{r} + A_3 \right. \\ &\quad \left. = +B_3 \cdot \frac{1}{r^3} + \frac{\varepsilon X}{2\pi\eta\varkappa^2} \cdot \frac{1}{r} \cdot \frac{\mathrm{d}\varphi}{\mathrm{d}r} \right] \cdot \cos(\vartheta) \,, \\ \mathfrak{v}_\vartheta &= \left[-\frac{A_1}{\eta} \cdot \frac{r^2}{5} - \frac{B_1}{2\eta} \cdot \frac{1}{r} - A_3 \right. \\ &\quad \left. = +\frac{B_3}{2} \cdot \frac{1}{r^3} - \frac{\varepsilon X}{4\pi\eta\varkappa^2} \cdot \frac{1}{r} \cdot \frac{\mathrm{d}}{\mathrm{d}r} r \cdot \frac{\mathrm{d}\varphi}{\mathrm{d}r} \right] \cdot \sin(\vartheta) \,, \\ \mathfrak{v}_\varphi &= 0 \,, \\ p &= A_0 + \left[A_1 r + \frac{B_1}{r^2} - \frac{\varepsilon X}{4\pi} \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r} \right] \cdot \cos(\vartheta) \,. \end{aligned}\right\} \tag{3.17}$$

3.3. Fulfillment of Boundary Conditions. Total Transmitted Force

According to our assumption, the velocity at a large distance should be parallel to the x axis and have the magnitude $-v$. This means that $\mathfrak{v}_r$ and $\mathfrak{v}_\vartheta$ should

asymptotically result in

$$\begin{aligned}\mathfrak{v}_r &= -v \cdot \cos(\vartheta)\,,\\ \mathfrak{v}_\vartheta &= v \cdot \sin(\vartheta)\,.\end{aligned}$$

The comparison with Equation 3.17 shows that

$$\begin{aligned}A_1 &= 0\,,\\ A_3 &= -v\end{aligned}$$

Now, apart from A_0, a constant that is only relevant for the absolute determination of the pressure and can therefore be set equal to 0 without any restrictions, B_1 and B_3 can also be chosen arbitrarily. They are determined by the condition that at the surface of the sphere (with radius b) both $\mathfrak{v}_r$ and $\mathfrak{v}_\vartheta$ must vanish and therefore result from the two equations:

$$\left.\begin{aligned}&\frac{B_1}{\eta}\cdot\frac{2}{b} + B_3\cdot\left(\frac{2}{b}\right)^3\\ &= v - \frac{\varepsilon X}{2\pi\eta\varkappa^2}\cdot\left(\frac{1}{r}\cdot\frac{\mathrm{d}\psi}{\mathrm{d}r}\right)_{r=b}\,,\\ &\frac{B_1}{\eta}\cdot\frac{2}{b} - B_3\cdot\left(\frac{2}{b}\right)^3\\ &= 2v - \frac{\varepsilon X}{2\pi\eta\varkappa^2}\cdot\left(\frac{1}{r}\cdot\frac{\mathrm{d}}{\mathrm{d}r}r\cdot\frac{\mathrm{d}\psi}{\mathrm{d}r}\right)_{r=b}\,.\end{aligned}\right\} \tag{3.18}$$

Taking into account the differential equation for ψ, one finds:

$$\left.\begin{aligned}\frac{B_1}{\eta}\cdot\frac{2}{b} &= +\frac{3}{2}\cdot v - \frac{\varepsilon X}{4\pi\eta}\cdot(\psi)_{r=b}\,,\\ B_3\cdot\left(\frac{2}{b}\right)^3 &= -\frac{1}{2}\cdot v + \frac{\varepsilon X}{4\pi\eta}\cdot\left(\frac{\mathrm{d}^2\psi}{\mathrm{d}(\varkappa r)^2}\right)_{r=b}\,.\end{aligned}\right\} \tag{3.18'}$$

All available constants are now determined and the stresses transmitted through any surface element can now be calculated. The force transmitted to the sphere will be directed in the x direction, it is transmitted through the surface elements of the sphere, whose normal is always r. We are therefore looking for the stress components, which are denoted by p_{rx} according to the usual notation.

The following holds:

$$p_{rx} = p_{xx}\cdot\frac{x}{r} + p_{yx}\cdot\frac{y}{r} + p_{zx}\cdot\frac{z}{r}\,;$$

furthermore

$$p_{xx} = -p + 2\eta \cdot \frac{\partial \mathfrak{v}_x}{\partial x}\,,$$
$$p_{yx} = \eta \cdot \left(\frac{\partial \mathfrak{v}_y}{\partial x} + \frac{\partial \mathfrak{v}_x}{\partial y}\right)\,,$$
$$p_{zx} = \eta \cdot \left(\frac{\partial \mathfrak{v}_z}{\partial x} + \frac{\partial \mathfrak{v}_x}{\partial z}\right)\,;$$

applies and finally

$$\mathfrak{v}_x = \mathfrak{v}_r \cdot \cos(\vartheta) - \mathfrak{v}_\vartheta \cdot \sin(\vartheta)\,,$$
$$\mathfrak{v}_y = [\mathfrak{v}_r \cdot \sin(\vartheta) + \mathfrak{v}_\vartheta \cdot \cos(\vartheta)] \cdot \cos(\varphi)\,,$$
$$\mathfrak{v}_z = [\mathfrak{v}_r \cdot \sin(\vartheta) + \mathfrak{v}_\vartheta \cdot \cos(\vartheta)] \cdot \sin(\varphi)\,.$$

Using a somewhat longer but elementary calculation, one can determine p_{rx} based on the expressions given in Equation 3.17 for $\mathfrak{v}$ and p. So with $A_0 = 0$ and using the differential equation for ψ it follows that:

$$\left.\begin{aligned} p_{rx} &= \left[\left(B_3 \cdot \frac{3}{r^4} + \frac{\varepsilon X}{4\pi\eta\varkappa^2} \cdot \frac{\mathrm{d}^3\psi}{\mathrm{d}r^3}\right)\right. \\ &= -\left(\frac{B_1}{\eta} \cdot \frac{3}{r^2} + B_3 \cdot \frac{9}{r^4} - \frac{6\varepsilon X}{4\pi\eta\varkappa^2} \cdot \left(\frac{1}{r} \cdot \frac{\mathrm{d}^2\psi}{\mathrm{d}r^2}\right.\right. \\ &= \left.\left.\left.-\frac{1}{r^2} \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r}\right)\right) \cdot \cos^2(\vartheta)\right]\,. \end{aligned}\right\} \tag{3.19}$$

The force transmitted to a sphere of radius r in the x direction follows by integrating p_{rx} over the surface of the sphere with the area element $\mathrm{d}\zeta$ and yields

$$\int p_{rx}\,\mathrm{d}\zeta = 4\pi\eta \cdot \left[-\frac{B_1}{\eta} + \frac{\varepsilon X}{4\pi\eta} \cdot r^2 \cdot \frac{\mathrm{d}\psi}{\mathrm{d}r}\right]\,. \tag{3.20}$$

Now the value of the constant B_1 from Equation 3.18' can be inserted and $r = b$ can be set. One finds

$$\int p_{rx}\,\mathrm{d}\zeta = -6\pi\eta v b + \varepsilon X b \cdot \left[\frac{\mathrm{d}}{\mathrm{d}r}(r\psi)\right]_{r=b}\,. \tag{3.20'}$$

Finally, the previously determined expression for the electrical potential ψ around an ion with charge q_j

$$\psi = \frac{q_j}{\varepsilon} \cdot \frac{e^{-\varkappa \cdot r}}{r}\,,$$

which is correct for small concentrations, can now be used for the final calculation.

This gives the force K_x transferred to the ion of radius b in the x direction:

$$K_x = -6\pi\eta v b - q_j X \varkappa b\,. \tag{3.21}$$

One can therefore see how, in addition to the STOKES force

$$6\pi\eta v b$$

there is an additional force resulting from electrophoresis, which also increases with increasing $\varkappa$, i.e. increasing concentration. The ratio of this additional force to the force $q_j \cdot X$ acting on the ion in the pure solvent is

$$\varkappa \cdot b\,,$$

is therefore equal to the ratio of the ionic radius to the average thickness of the ionic cloud. For an aqueous solution of a uni-univalent salt, for example, we found earlier

$$\varkappa = 0.326 \cdot 10^8 \cdot \sqrt{\gamma}\,,$$

where γ is the concentration in moles per liter. So in this case that ratio can be calculated as

$$\varkappa \cdot b = 0.326 \cdot 10^8 \cdot b \cdot \sqrt{\gamma}$$

and since b is of the order 1×10^{-8} cm, one sees that also the electrophoretic forces, like those already discussed earlier ionic forces become significant even at small concentrations. In the fact that both forces are proportional to the square root of the concentration (as long as one restricts oneself to the limiting case of small concentrations) one is aware of the reason why this square root also plays a role in conductivity. But the fact that the forces show this proportionality is based on the fact that the thickness of the ionic cloud is inversely proportional to the square root of the concentration and this was ultimately a consequence of the square distance law of COULOMB, which causes the mutual force effect of the ions.

4. Conductivity

4.1. The Coefficient of Conductivity

The external field strength X acts in the x direction on an ion with charge q_j. This is contained in a solution in which each cm^3 contains

$$n_1, \ldots \quad n_i, \ldots \quad n_s$$

ions[1] with charges

$$q_1, \ldots \quad q_i, \ldots \quad q_s \,.$$

As a result of the finite relaxation time, which is required by the ionic cloud that is constantly being formed during the transport of the ion, the amount

$$-\frac{\omega_j \varkappa}{6} \cdot \frac{q_j^2}{\varepsilon}$$

is added to the force $q_j \cdot X$ according to Equation 2.18. The total force

$$q_j \cdot X - \frac{\omega_j \varkappa}{6} \cdot \frac{q_j^2}{\varepsilon} \tag{4.1}$$

tries to set the ion in motion and causes such a velocity that the total friction force is kept in balance. However, as a result of electrophoretic effects, the total friction force is greater than that which can be calculated using the STOKES formula, namely according to Equation 3.21 it is equal to

$$-6\pi\eta b_j v_j - q_j X \varkappa b_j \,, \tag{4.2}$$

if the velocity of the ion is now v_j and its radius is denoted by b_j. It is determined from the condition that the total force is zero, i.e. from the equation

$$q_j \cdot X - \frac{\omega_j \varkappa}{6} \cdot \frac{q_j^2}{\varepsilon} - 6\pi\eta b_j v_j - q_j X \varkappa b_j = 0 \,. \tag{4.3}$$

[1] In chapter 2 we have denoted the same quantities $\overline{n_i}$; However, in the following we can leave out the line without ambiguity.

According to chapter 2 the size ω_j is an abbreviation for

$$\omega_j = \frac{\xi v_j}{k_\mathrm{B} T} \,.$$

Furthermore, the average friction constant ξ is composed of the individual friction constants ξ_i according to the formula

$$\xi = \frac{\sum_i n_i q_i^2 \xi_i}{\sum_i n_i q_i^2} \,, \tag{4.4}$$

while finally $\varkappa$ has the previous meaning (see Equation 4.2), according to which

$$\varkappa^2 = \frac{4\pi}{\varepsilon k_\mathrm{B} T} \cdot \sum_i n_i q_i^2 \,. \tag{4.5}$$

For an infinitely small concentration $\varkappa = 0$, then

$$e_j \cdot X - 6\pi\eta b_j v_j = 0$$

would be, so that the velocity can be calculated according to the usual equation, in which the equation

$$6\pi\eta b_j = \xi_j$$

can be set because of the introduced meaning of ξ_j. If this is taken into account, it follows from Equation 4.3 in the second approximation, i.e. for finite concentrations

$$v_j = \frac{q_j X}{\xi_j} \cdot \left[1 - \frac{\xi}{\xi_j} \cdot \frac{q_j^2 \varkappa}{6\varepsilon k_\mathrm{B} T} - b_j \varkappa \right] \,. \tag{4.6}$$

Now, as is well known, the specific conductivity λ (in the electrostatic system) is determined by the formula[2]

$$\lambda = \frac{1}{X} \cdot \sum_j n_j q_j v_j \,,$$

and therefore using Equation 4.6 it follows:

$$\lambda = \sum_j \frac{n_j q_j^2}{\xi_j} - \varkappa \cdot \left[\sum_j \frac{n_j q_j^4}{6\varepsilon k_\mathrm{B} T} \cdot \frac{\xi}{\xi_j^2} + \sum_j \frac{n_j q_j^3}{\xi_j} \cdot b_j \right] \,. \tag{4.7}$$

[2]The SI unit of λ results from the following calculation: X is the external field strength and has the unit $\frac{\mathrm{V}}{\mathrm{m}}$ or $\frac{\mathrm{N}}{\mathrm{C}}$. So it follows that λ has the unit $\frac{1}{\frac{\mathrm{N}}{\mathrm{C}}} \cdot \frac{1}{\mathrm{m}^3} \cdot \mathrm{C} \cdot \frac{\mathrm{m}}{\mathrm{s}}$. If we write N (Newton) as $\frac{\mathrm{kg\,m}}{\mathrm{s}^2}$, $\mathrm{C} = \mathrm{A\,s}$ we get $\frac{\mathrm{A}^2\,\mathrm{s}^3}{\mathrm{kg\,m}^3}$, which bearing in mind that Ω equals $\frac{\mathrm{kg\,m}^2}{\mathrm{s}^3\,\mathrm{A}^2}$ results after summarising the unit of Ω in the SI unit $\frac{1}{\Omega\,\mathrm{m}}$ or, as $1\,\mathrm{S} = 1\,\Omega^{-1}$ in $\mathrm{S\,m}^{-1}$.

Let the specific conductivity at infinitesimal dilution be called λ_0, then

$$\lambda_0 = \sum_j \frac{n_j q_j^2}{\xi_j} .$$

Furthermore, the conductivity coefficient f_λ is defined by the Ansatz

$$f_\lambda = \frac{\lambda_0 - \lambda}{\lambda_0} ,$$

so that, as usual, it measures the relative change in conductivity with increasing concentration. If one then takes into account the definition equations according to Equation 4.4 and Equation 4.5 for the mean ξ and for $\varkappa$ and consistently writes i instead of j for the summation index, then it follows that

$$\left.\begin{aligned} 1 - f_\lambda = & \sqrt{\frac{4\pi}{\varepsilon k_\mathrm{B} T} \cdot \sum_i n_i q_i^2} \\ & \cdot \left\{ \frac{\sum_i n_i q_i^2 \xi}{\sum_i n_i q_i^2} \cdot \frac{\sum_i \frac{n_i q_i^4}{6\varepsilon k_\mathrm{B} T} \cdot \frac{1}{\xi_i^2}}{\sum_i \frac{n_i q_i^2}{\xi_i}} + \frac{\sum_i \frac{n_i q_i^2}{\xi_i} \cdot b_i}{\sum_i \frac{n_i q_i^2}{\xi_i}} \right\} . \end{aligned}\right\} \tag{4.8}$$

In Equation 4.8 no prerequisite is made about the particular type of dissolved substances, so the formula can also be used, for example, on mixtures. However, it is often the case that n molecules of a single salt are dissolved in a cm^3. If each of these molecules decays into

$$\nu_1, \ldots \quad \nu_i, \ldots \quad \nu_s$$

ions with the valence

$$z_1, \ldots \quad z_i, \ldots \quad z_s$$

and the charge of an electron is denoted by e_0, then in this special case Equation 4.8 takes the form:

$$1 - f_\lambda = \sqrt{\frac{4\pi e_0^2}{\varepsilon k_\mathrm{B} T} \cdot \nu n} \cdot \left\{ \frac{e_0^2}{6\varepsilon k_\mathrm{B} T} \cdot w_1 + b \cdot w_2 \right\} . \tag{4.9}$$

Here

$$\nu = \sum_i \nu_i \tag{4.9'}$$

is set, which means the total number of ions into which a molecule decomposes, while w_1 and w_2 are numbers that we want to call valence factors. These are

defined by the equations:

$$\left.\begin{aligned} w_1 &= \frac{\sum_i \nu_i z_i^2 \xi_i}{\sqrt{\nu \cdot \sum_i \nu_i z_i^2}} \cdot \frac{\sum_i \frac{\nu_i z_i^4}{\xi^2}}{\sum_i \frac{\nu_i z_i^2}{\xi_i}}\,, \\ w_2 &= \sqrt{\frac{\nu_i z_i^2}{\nu}}\,. \end{aligned}\right\} \tag{4.9"}$$

In addition, instead of the ionic diameter b_i, an average diameter b is introduced using the defining equation

$$b = \frac{\sum_i \frac{\nu_i z_i^2}{\xi_i} \cdot b_i}{\sum_i \frac{\nu_i z_i^2}{\xi_i}}\,. \tag{4.9"'}$$

4.2. Discussion of the Coefficient of Conductivity

According to Equation 4.9 $1 - f_\lambda$ is proportional to $\sqrt{n}$, i.e. proportional to the square root of the concentration. The theory therefore confirms KOHLRAUSCH's law, which was already highlighted in the introduction.

Secondly, Equation 4.9 shows that $1 - f_\lambda$ is linked to the dielectric constant ε of the solvent. The dependency is not a simple one, since the expression of $1 - f_\lambda$ is composed of two summands, one of which is proportional to $\varepsilon^{\frac{3}{2}}$ and the other is proportional to $\varepsilon^{\frac{1}{2}}$. Here we can only state that the theory requires larger deviations from the limiting conductivity for a given concentration, the smaller the dielectric constant of the solvent. But this is in qualitative agreement with the experimental findings of WALDEN, whose rule will only be discussed in more detail in chapter 5.

If one has aqueous solutions and refers to 18 °C, then according to the DRUDE formula, [12], the following holds good (t = temperature °C):

$$\varepsilon = 88.23 - 0.4044 \cdot t + 0.001035 \cdot t^2\,,$$

from which at 18 °C follows

$$\varepsilon = 81.29\,.$$

If one continues to set $\varepsilon = 4.77 \times 10^{-10}\,\mathrm{statC}$, $k_\mathrm{B} = 1.346 \times 10^{-16}\,\mathrm{erg\,Grad^{-1}}$, $T = 291\,\mathrm{K}$, and denote the concentration of the salt in moles per liter as γ, so that

$$n = 6.06 \cdot 10^{20} \cdot \gamma\,,$$

then the factors can be calculated in Equation 4.9 and one obtains for aqueous

solutions:

$$1 - f_\lambda = \left[0,278 \cdot w_1 + 0,233 \cdot 10^8 \cdot b w_2\right] \cdot \sqrt{\nu\gamma}\,. \tag{4.10}$$

It is now interesting to compare the conductivity coefficient f_λ with the osmotic coefficient f_0 found earlier. Based on water of 18 °C one finds according to the previous information

$$1 - f_\lambda = 0.278 \cdot w \cdot \sqrt{\nu\gamma}\,, \tag{4.11}$$

where the valence factor determining the osmotic coefficient was

$$w = \left(\frac{\sum_i \nu_i z_i^2}{\nu}\right)^{\frac{3}{2}}\,, \tag{4.11'}$$

So one can see that there is actually a connection between f_λ and f_0, but it is not a simple one and, above all, there is no way to infer f_0 from f_λ other than by order of magnitude. The two reasons that prevent this are, firstly, that the valence factor w in f_0 can actually be determined using the valences alone, while the valence factor w_1 in f_1, determined according to Equation 4.9" still contains the conditions of mobility. Secondly, as e.g. Equation 4.10 shows, in order to calculate f_λ, knowledge of the mean ion diameter b is required, what then, if one e.g. considers the relationship derived from Stokes' law

$$\xi_i = 6\pi\eta b_i$$

to be correct, in turn means that the mobilities are also decisive for the calculation of the second term in f_λ. We believe that incidentally from a physical point of view it is obvious from the outset to consider the opposite claim by Ghosh, according to whom f_0 and f_λ are readily mutually dependent in their magnitude, to be unlikely.

The characteristic difference between the behavior of f_0 and f_λ can also be shown as follows. Since the expression for f_0 only contains the disintegration numbers ν_i and the valences z_i, all salts that decompose similarly must produce the same deviations from the classically calculated osmotic pressure in the limit for small concentrations. On the other hand, since f_λ also contains the mobilities, the deviations of the conductivity from its limit value, even in the limit for small concentrations and for similarly disintegrating salts, must still exhibit individual differences. In chapter 5 we will be able to show using experimental data that this is indeed the case and that the opposite claim of Ghosh's theory is also not true in practice.

Some data for the valence factors w_1 and w_2 have now been compiled, namely for the 3 salt types KCl, K_2SO_4 and $MgSO_4$. The following Table 4.1 contains the information for w_2.

type of salt	w_2
KCl	$\sqrt{1}$=1
K_2SO_4 ...	$\sqrt{2}$ =1.414
$MgSO_4$ ...	$\sqrt{4}$=4

Table 4.1.: Values of the valence factor w_2 for different types of salts

The valence factor w_1 is still a function of the mobilities and, as can be seen immediately, it only contains their ratios.

(a) *For uni-univalent salts* (of type KCl) it follows

$$w_1 = \frac{\xi_1 + \xi_2}{2} \cdot \frac{\frac{1}{\xi_1^2} + \frac{1}{\xi_2^2}}{\frac{1}{\xi_1} + \frac{1}{\xi_2}} \,. \tag{4.12}$$

If one also sets

$$\left.\begin{aligned} \phi_1 &= \frac{\xi_1}{\xi_1 + \xi_2} \,, \\ \phi_2 &= \frac{\xi_2}{\xi_1 + \xi_2} \,, \end{aligned}\right\} \tag{4.13}$$

so that

$$\phi_1 + \phi_2 = 1$$

and the ϕ are pure integers, then the following holds good:

$$w_1 = \frac{1}{2} \cdot \frac{\phi_1^2 + \phi_2^2}{\phi_1 \cdot \phi_2} = \frac{1}{2} \cdot \left(\frac{\phi_1}{\phi_2} + \frac{\phi_2}{\phi_1} \right) \,. \tag{4.14}$$

If the friction constants are the same, $\phi_1 = \phi_2$ and w_1 becomes equal to 1. If the friction constants are different, then $w_1 > 1$. The more different the mobilities are, the larger the first term in $1 - f_\lambda$ becomes. Table 4.2 provides information about the values of w_1 at different ratios ϕ for uni-univalent salts. The minimum is reached for $\phi_1 = \phi_2$.

ϕ_1	ϕ_2	w_1
0.1	0.9	4.55
0.2	0.8	2.12
0.3	0.7	1.38
0.4	0.6	1.08
0.5	0.5	1.00
0.6	0.4	1.08
0.7	0.3	1.38
0.8	0.2	2.12
0.9	0.1	4.55

Table 4.2.: Type KCl. Values of the valence factor w_1 in dependence of different relations of ϕ

(b) *For di-univalent salts* (of type K_2SO_4) the result is similar

$$\left.\begin{aligned} w_1 &= \frac{2\xi_1 + 4\xi_2}{3\sqrt{2}} \cdot \frac{\frac{2}{\xi_1^2} + \frac{16}{\xi_2^2}}{\frac{2}{\xi_1} + \frac{4}{\xi_2}} \\ &= \frac{\sqrt{2}}{3} \cdot \frac{\phi_1 + 2\phi_2}{2\phi_1 + \phi_2} \cdot \left(8 \cdot \frac{\phi_1}{\phi_2} + \frac{\phi_2}{\phi_1}\right) . \end{aligned}\right\} \qquad (4.14')$$

The index 1 refers to the monovalent ion, the index 2 to the divalent ion. Table 4.3 provides information about the numerical values. The minimum with $w_1 = 3.53$ is reached at $\phi_1 = 0.48 \cdot \phi_2$.

(c) Finally, the following formula applies to divalent salts (type $MgSO_4$):

$$w_1 = 4 \cdot (\xi_1 + \xi_2) \cdot \frac{\frac{1}{\xi_1^2} + \frac{1}{\xi_2^2}}{\frac{1}{\xi_1} + \frac{1}{\xi_2}} = 4 \cdot \left(\frac{\phi_1}{\phi_2} + \frac{\phi_2}{\phi_1}\right) , \qquad (4.14")$$

so that in this case the values for the valence factor are simply 8 times the numbers given in Table 4.2. The minimum values of the valence factors w_1 are therefore 1, 3.53 and 8 for the three salt types mentioned.

The theoretically required strong increase of $1 - f_\lambda$ with increasing valence is qualitatively in agreement with the finding that, at the same equivalent concentration,

ϕ_1	ϕ_2	w_1
0.1	0.9	8.05
0.2	0.8	4.24
0.3	0.7	3.55
0.4	0.6	3.68
0.5	0.5	4.24
0.6	0.4	5.22
0.7	0.3	6.87
0.8	0.2	10.1
0.9	0.1	18.8

Table 4.3.: Type K_2SO_4. Values of the valence factor w_1 in dependence of different relations of ϕ

the deviations from the limiting conductivity are greater, the greater the valence of the dissolved ions.

5. Comparison with Empirics

5.1. Aqueous Solutions of uni-univalent Salts

In the case of uni-univalent salts, there is a relatively large and carefully examined material available for testing the limiting law, which we owe to the many years of work by KOHLRAUSCH. As is well known, it was this material on the basis of which KOHLRAUSCH, [42, 35], developed his law according to which

$$1 - f_\lambda \sim \sqrt{\gamma}\,.$$

KOHLRAUSCH's law is demonstrated very vividly by the well-known figure, also printed in the book by KOHLRAUSCH and HOLBORN, in which the equivalent conductivity is plotted as a function of the square root of the concentration. It is therefore completely unnecessary to say anything other than that the above developments mean that the law is now also theoretically justified. But what is also important is the numerical value of the proportionality constant.

In the following we will always calculate with the so-called *molecular conductivity* and not with the equivalent conductivity. The former shall be defined as the quotient of the specific conductivity λ and the number of moles $\gamma/1000$ dissolved in one cubic centimeter of solution. Incidentally, for uni-univalent salts, the molecular conductivity and equivalent conductivity are identical. To define the conductivity coefficient f_λ we set:

$$\lambda = \lambda_0 \cdot f_\lambda\,,$$

where λ_0 was the conductivity that the solution would exhibit if the ions moved as they do at infinitesimal dilution. It was therefore in general

$$\lambda_0 = \sum_i \frac{n_i q_i^2}{\xi_i}\,.$$

If there are dissolved n molecules of a salt in one cubic centimeter, each of which disintegrates into

$$\nu_1, \ldots \nu_i, \ldots \nu_s$$

ions with valences

$$z_1, \ldots z_i, \ldots z_s\,,$$

the following holds good:

$$\lambda_0 = ne_0^2 \cdot \sum_i \frac{\nu_i z_i^2}{\xi_i},$$

if e_0 is the charge of an electron. Now

$$n = N_A \cdot \frac{\gamma}{1000},$$

if $N_A = 6.06 \times 10^{23}\,\mathrm{mol}^{-1}$ means the AVOGADRO constant. If we denote the molecular conductivity by Λ_m, then

$$\Lambda_\mathrm{m} = \frac{1000 \cdot \lambda}{\gamma} = f_\lambda N_A e_0^2 \cdot \sum_i \frac{\nu_i z_i^2}{\xi_i}; \tag{5.1}$$

The molecular conductivity at infinitesimal dilution shall be denoted by Λ_m^0 and is equal to

$$\Lambda_\mathrm{m}^0 = N_A e_0^2 \cdot \sum_i \frac{\nu_i z_i^2}{\xi_i}. \tag{5.1'}$$

Now it is not customary to express Λ_m and Λ_m^0 in electrostatic units as in these formulæ. Rather, the unit $\mathrm{cm}^2\,\Omega^{-1}$ was chosen. Expressed in these practical units, let the conductivities be denoted by $\overline{\Lambda}_\mathrm{m}$ and $\overline{\Lambda}_\mathrm{m}^0$. Then

$$\overline{\Lambda}_\mathrm{m} = \frac{\Lambda_\mathrm{m}}{9 \cdot 10^{11}}$$

and

$$\overline{\Lambda}_\mathrm{m}^0 = \frac{\Lambda_\mathrm{m}^0}{9 \cdot 10^{11}};$$

The information in the following tables refers entirely to these practical units.

The root law is just a limiting law, from which the deviations increase with increasing concentration. We therefore took the values of $\overline{\Lambda}_\mathrm{m}$ given by KOHLRAUSCH, [36, 39], for the six smallest concentrations at which measurements are available, namely $\gamma = 0.0001$, 0.0002, 0.0005, 0.001, 0.002 and 0.005 and have $\overline{\Lambda}_\mathrm{m}$ represented by a formula:

$$\overline{\Lambda}_\mathrm{m} = \overline{\Lambda}_\mathrm{m}^0 - \alpha \cdot \sqrt{2\gamma} + \beta \cdot (2\gamma), \tag{5.2}$$

where the coefficients $\overline{\Lambda}_\mathrm{m}^0$, α and β were determined using the least squares method, respectively. The adaption to the empirical value of $\overline{\Lambda}_\mathrm{m}$ is very good for the uni-univalent salts, as can be seen from the following Table 5.1, which refers, for example, to KCl solutions:

The first and second columns contain 2γ and $\sqrt{2\gamma}$, the third column contains

2γ	$\sqrt{2\gamma}$	$\overline{\Lambda}_{\mathrm{m,\,calc.}}$	$\overline{\Lambda}_{\mathrm{m,\,obs.}}$	Δ
0.0002	0.014 142	129.09	129.07	−0.02
0.0004	0.020 000	128.75	128.77	0.02
0.0010	0.031 623	128.08	128.11	0.03
0.0020	0.044 721	127.34	127.34	0.00
0.0040	0.063 246	126.32	126.31	−0.01
0.0100	0.100 000	124.39	124.41	0.02
0.0200	0.141 42	122.36	122.43	0.07
0.0400	0.200 00	119.75	119.96	0.21
0.1000	0.316 23	115.51	115.75	0.24

Table 5.1.: Calculated and observed values of molar conductivity $\overline{\Lambda}_{\mathrm{m}}$ of KCl solutions in dependence of different concentrations γ

the calculated molecular conductivity and the fourth column contains the observed molecular conductivity. The last column contains the difference between the last two values. The table is divided into 2 parts by a horizontal line, the range under the line was not used when calculating the three coefficients $\overline{\Lambda}^0_{\mathrm{m}}$, α and *beta*. The formula, which resulted from the least squares method and which underlies the values $\overline{\Lambda}_{\mathrm{m,\,calc.}}$, is:

$$\overline{\Lambda}_{\mathrm{m}} = 129.93 - 59.94 \cdot \sqrt{2\gamma} + 45.3 \cdot (2\gamma)\,.$$

The following Table 5.2 contains the chemical formula of the 18 salts calculated in this way in the first column. The second, third and fourth columns contain the values of $\overline{\Lambda}^0_{\mathrm{m}}$, α and β. The fifth column contains the ratio $\alpha/\overline{\Lambda}^0_{\mathrm{m}}$. The values apply to a temperature of 18 °C.

It is still of interest to compare Kohlrausch's measurements with those of another researcher. Figure 5.1 is designed for this purpose. Plotted as a function of $\sqrt{2\gamma}$, it contains, firstly, the conductivities of KCl solutions observed by Kohlrausch as black big circles, as well as the regression line of Table 5.2:

$$\overline{\Lambda}_{\mathrm{m}} = 129,93 - 59,94 \cdot \sqrt{2\gamma}\,.$$

In addition, observations from Weiland, [62], which extend over the concentration range $\gamma = 10^{-5}$ to $\gamma = 10^{-3}$, are entered as small red circles. One probably has the

type of salt	$\overline{\Lambda}^0_m$	α	β	$\alpha/\overline{\Lambda}^0_m$	$0.278 \cdot w_1$	$10^8 \cdot b$
LiCl	98.93	57.35	71.4	0.580	0.342	1.02
$LiIO_3$	67.35	48.33	36.6	0.718	0.278	1.89
$LiNO_3$	95.24	56.27	71.5	0.591	6.332	1.11
NaF	90.05	50.42	23.1	0.560	0.278	1.20
NaCl	108.89	54.69	34.9	0.502	0.301	0.85
$NaIO_3$	77.42	51.39	34.2	0.664	0.286	1.62
$NaNO_3$ ...	105.34	58.27	52.7	0.553	0.295	1.11
KF	111.29	55.88	44.9	0.502	0.292	0.90
KCl	129.93	59.94	45.3	0.461	0.278	0.79
KBr	132.04	62.17	55.9	0.471	0.278	0.83
KI	130.52	51.53	−16.6	0.395	0.278	0.50
KIO_3	98.41	54.18	19.6	0.551	0.338	0.92
$KClO_3$ ...	119.47	58.16	14.4	0.487	0.281	0.88
KNO_3	126.46	65.67	59.3	0.519	0.278	1.04
KCNS	121.04	54.10	10.9	0.447	0.281	0.71
CsCl	133.08	53.75	−26.4	0.404	0.278	0.54
$AgNO_3$ ...	115.82	62.35	43.2	0.538	0.281	1.19
$TlNO_3$ ...	127.55	63.40	−14.1	0.497	0.279	0.94

Table 5.2.: Calculated values of $\overline{\Lambda}^0_m$, α and β of 18 different salts according to the least squares method

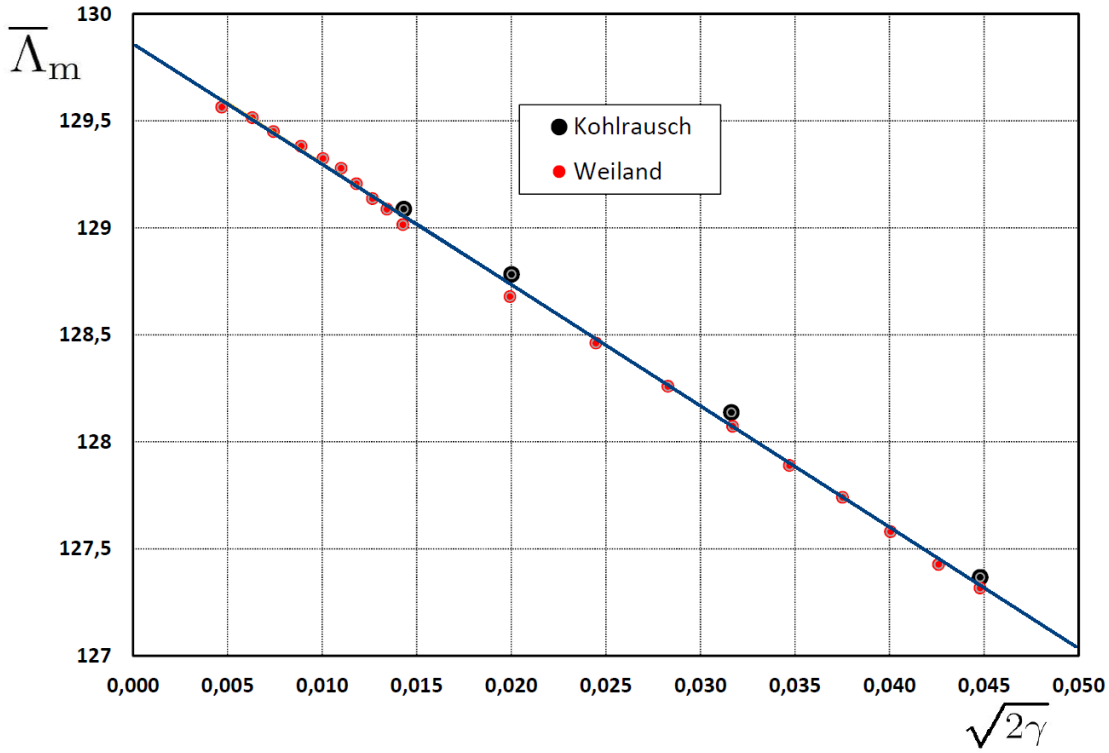

Figure 5.1.: Comparison of KOHLRAUSCH's measurements with those of WALDEN for KCl in H_2O

impression that the KOHLRAUSCH values are excellently validated.

Of particular interest to us is the ratio $\alpha/\overline{\Lambda}_m^0$ of the fifth column. According to the definition of f_λ

$$1 - f_\lambda = \frac{\alpha}{\overline{\Lambda}_m^0} \cdot \sqrt{2\gamma}\,.$$

The table now shows how $\alpha/\overline{\Lambda}_m^0$ varies between 0.395 for KI and 0.718 for $LiIO_3$. There can therefore be no question of the limiting law being the same for all uni-univalent salts, as would be expected according to GHOSH's theory. According to the theory presented here, the relationship should exist according to Equation 4.10:

$$1 - f_\lambda = \left[0.278 \cdot w_1 + 0.233 \cdot 10^8 \cdot b\right] \cdot \sqrt{2\gamma}\,,$$

where w_2 was set equal to 1 according to Table 4.1, but the valence factor w_1 is to be calculated according to Equation 4.12 or Equation 4.14 and therefore still depends on the ratio of the two mobilities. As the mobilities L_i we define the

	Li	Na	K	Cs	Ag	Tl	F
$\overline{L} =$	33,46	43,49	64,61	67,69	43,99	65,72	46,62
	Cl	Br	I	ClO_3	IO_3	NO_3	CNS
$\overline{L} =$	65,39	67,43	65,91	54,86	33,87	61,83	56,43

Table 5.3.: Mobility of different kinds of univalent ions (cations and anions)

contributions affecting an ion in Equation 5.1', so that

$$L_i = N_A e_0^2 \cdot \frac{z_i^2}{\xi_i} \tag{5.3}$$

and thus

$$\Lambda_{\mathrm{m}}^0 = \sum_i \nu_i L_i \,. \tag{5.4}$$

Measured in the practical system, the mobilities are again denoted by $\overline{L}$, so that

$$\overline{L_i} = \frac{L_i}{9 \cdot 10^{11}} \,.$$

According to Equation 4.14 we then have

$$w_1 = \frac{1}{2} \cdot \left(\frac{L_2}{L_1} + \frac{L_1}{L_2} \right) \,. \tag{5.5}$$

We considered it advisable to use a material that was as homogeneous as possible and therefore recalculated the mobilities based on the limiting conductivity values $\overline{\Lambda}_{\mathrm{m}}^0$ given in Table 5.2. The ratio of the transport numbers, [37, 44], of K and Cl to 0.497 : 0.503 was assumed to be absolutely precise. Then the mobilities of the individual ions were calculated so that the sum of the squares of the deviations of the limit conductivities to be calculated using the mobilities from the $\overline{\Lambda}_{\mathrm{m}}^0$-values of Table 5.2 became a minimum. This resulted in Table 5.3.

The following Table 5.4 provides information about the $\overline{\Lambda}_{\mathrm{m}}^0$ values to be calculated with the help of these mobilities. The last column shows the deviations Δ in percent. If the calculated $\overline{\Lambda}_{\mathrm{m}}^0$ values are in brackets, this means that the salt contains an ion that only appears once in the table, a Δ value is then inherently non-existent.

What is denoted in the table by $\overline{\Lambda}_{\mathrm{m,\,obs.}}^0$ is the value that is calculated based on the experimental data using Equation 5.2, while $\overline{\Lambda}_{\mathrm{m,\,calc.}}^0$ is the value obtained by appropriate addition (according to Equation 5.4) from the $\overline{L}$ values given above.

Salt	$\overline{\Lambda}^0_{\mathrm{m,\,obs.}}$	$\overline{\Lambda}^0_{\mathrm{m,\,calc.}}$	Δ percent
LiCl ..	98.93	98.85	0.08
$LiIO_3$.	67.35	67.33	0.03
$LiNO_3$	95.24	95.29	0.05
NaF ..	90.05	90.11	0.07
NaCl ..	108.89	108.88	0.01
$NaIO_3$	77.42	77.36	0.08
$NaNO_3$	105.34	105.32	0.02
KF ...	111.29	111.23	0.05
KCl ...	129.93	130.00	0.05
KBr ..	132.04	(132,04)	–
KI	130.52	(130,52)	–
KIO_3 .	98.41	98.48	0.07
$KClO_3$	119.47	(119,47)	–
KNO_3 .	126.46	126.44	−0.02
KCNS	121.04	(121,04)	–
CsCl ..	133.08	(133,08)	–
$AgNO_3$	115.82	(115,82)	–
$TlNO_3$	127.55	(127,55)	–

Table 5.4.: Calculated and observed values of the limiting molar conductivity $\overline{\Lambda}^0_{\mathrm{m}}$ of 18 different types of salts

The valence factor w_1 was now calculated for each individual salt according to Equation 5.5. The first summand of $1 - f_\lambda$ is equal to $0.278 \cdot w_1$ as stated above. The numbers calculated with this value are entered in the 6th column of Table 5.2. One can see that these are always smaller than the experimentally determined gradient divided by $\overline{\Lambda}^0_\mathrm{m}$, i.e. $\alpha/\overline{\Lambda}^0_\mathrm{m}$. This means that the ionic effect does not contribute to the entire reduction in conductivity; One will look for the deviation in the second term $1 - f_\lambda$, which comes from electrophoresis. If this is done, this deviation must be equal to $0.233 \cdot 10^8 \cdot b$ and we get the values for $10^8 \cdot b$ that are entered in column 7 of Table 5.2. Since the electrophoresis was calculated using the usual hydrodynamic equations, these values of the sphere radii will not be given too much weight. However, it corresponds to the expectation that the b values are all of the order 1×10^{-8} cm.

Finally, it should be noted that of the salts measured by Kohlrausch, the NH_4 salts were not taken into account because the accuracy of the measurements is lower. In addition, TlF was omitted because the experimental values show a maximum and could therefore not be represented by our limiting formula. The maximum is always more or less pronounced for the acids and bases. It is very likely that this maximum does not correspond to reality, at least in that case, and Kohlrausch himself is of this opinion. Strong support for this view is provided by recent measurements by Kraus and Parker, [45], who examined HIO_3 in vessels namely made of glass, Pyrex glass and quartz and observed the maximum coming less and less pronounced. However, it did not disappear even in quartz vessels, but according to these experiments it seems very doubtful whether the very difficult measurements at large dilutions can be viewed as definitive.

5.2. Aqueous Solutions of Salts with Polyvalent Ions

5.2.1. Mono- and Divalent Salts

Measurements from Kohlrausch are again used as a basis, namely on seven salts. The molecular conductivity (in this case twice the equivalent conductivity) is discussed using the same method as above. It was set

$$\overline{\Lambda}_\mathrm{m} = \overline{\Lambda}^0_\mathrm{m} - \alpha \cdot \sqrt{3\gamma} + \beta \cdot (3\gamma)$$

and from the observations at $\gamma = 0.00005$, $\gamma = 0.0001$, $\gamma = 0.00025$, $\gamma = 0.0005$ and $\gamma = 0.0010$ the coefficients $\overline{\Lambda}^0_\mathrm{m}$, α and β for each salt were determined by the least squares method. Table 5.5 gives an example for the case of $Ba(NO_3)_2$, for

3γ	$\sqrt{3\gamma}$	$\overline{\Lambda}^0_{\mathrm{m,\,calc.}}$	$\overline{\Lambda}^0_{\mathrm{m,\,obs.}}$	Δ
0.000 15	0.012 247	230.66	230.64	−0.01
0.000 30	0.017 321	229.30	229.30	0.00
0.000 75	0.027 386	226.58	226.60	0.01
0.001 50	0.038 730	223.46	223.44	−0.01
0.003 00	0.054 772	218.98	219.00	0.01
0.007 50	0.086 603	209.79	210.58	0.38
0.015 00	0.122 474	198.98	201.92	1.48
0.030 00	0.173 205	182.87	191.32	4.62
0.075 00	0.273 861	148.06	173.62	17.26

Table 5.5.: Calculated and observed values of the molar conductivity $\overline{\Lambda}_{\mathrm{m}}$ of $Ba(NO_3)_2$

which the formula resulted:

$$\overline{\Lambda}_{\mathrm{m}} = 233.90 - 262.23 \cdot \sqrt{3\gamma} - 187.0 \cdot (3\gamma)\,.$$

A horizontal line is drawn in the table; the interpolation formula refers to the area above the line. One can see how the numbers in this area are presented quite well, but outside of it larger deviations soon appear. The steeper course of the $\overline{\Lambda}_{\mathrm{m}}$ curve compared to that for uni-univalent salts means that the certainty with which α can be concluded is reduced. In addition, KOHLRAUSCH himself considers the measurements to be less reliable than those on uni-univalent salts, [38]. In this context we may perhaps note that where, as above in the case of $Ba(NO_3)_2$, the coefficient α is given with five-digits, this is only due to the fact that when carrying out the least squares method, the experimental numbers are considered to be absolutely accurate. However, the five-digit information is by no means to be regarded as having been experimentally validated with this level of accuracy.

Table 5.6 now contains the chemical formula of the salt and the values of $\overline{\Lambda}^0_{\mathrm{m}}$, α and β in the first four columns, in the fifth column there is further entered $\alpha/\overline{\Lambda}^0_{\mathrm{m}}$ (the limiting slope of the curve divided by $\overline{\Lambda}^0_{\mathrm{m}}$). The information refers to 18 °C. Experimentally,

$$1 - f_\lambda = \frac{\alpha}{\overline{\Lambda}^0_{\mathrm{m}}} \cdot \sqrt{3\gamma}$$

type of salt	$\overline{\Lambda}^0_m$	α	β	$\alpha/\overline{\Lambda}^0_m$	$0,278 \cdot w_1$	$10^8 \cdot b$
$Ba(NO_3)_2$	233.90	262.23	−187.0	1.121	0.986	0.41
$Sr(NO_3)_2$.	226.83	276.26	313.2	1.218	0.986	0.71
$CaCl_2$	233.38	248.69	110.7	1.066	0.992	0.23
$Ca(NO_3)_2$	227.11	275.50	327.7	1.213	0.982	0.70
$MgCl_2$	221.75	235.55	53.1	1.062	1.026	1.09
$Pb(NO_3)_2$	246.11	379.51	543.0	1.542	0.980	1.71
K_2SO_4 ...	264.46	229.04	−1488	0.866	0.980	–

Table 5.6.: Calculated values of $\overline{\Lambda}^0_m$, α and β of seven different types of uni-divalent salts

	Ba	Sr	Ca	Mg	Pb	SO_4
$\overline{L} =$	100,24	103,17	103,03	90,97	122,45	135,21

Table 5.7.: Mobility of different types of divalent ions

would be in the limit for small concentrations. Theoretically we found the Equation 4.10:

$$1 - f_\lambda = \left[0.278 \cdot w_1 + 0.233 \cdot 10^8 \cdot b w_2\right] \cdot \sqrt{3\gamma}\,,$$

since here $\nu = 3$. Furthermore, according to the general formula for w_1 in Equation 4.14' for the special case of mono-divalent salts

$$w_1 = \frac{2\xi_1 + 4\xi_2}{3\sqrt{2}} \cdot \frac{\frac{2}{\xi_1^2} + \frac{16}{\xi_2^2}}{\frac{2}{\xi_1} + \frac{4}{\xi_2}}$$

was given. First, the mobilities of the ions Ba, Sr, Ca, Mg, Pb and SO_4 were determined from the limiting conductivities $\overline{\Lambda}^0_m$ given in Table 5.6 using the numbers given in section 5.1 for NO_3 and Cl. The ion Ca occurs twice, from $Ca(NO_3)_2$ one finds its mobility $\overline{L} = 103.45$, from $CaCl_2$ on the other hand $\overline{L} = 102.60$, the average of these two numbers was assumed to be correct. In this way, Table 5.7 follows.

According to Equation 5.3,

$$L_i = N_A \cdot e_0^2 \cdot \frac{z_i^2}{\xi_i}$$

and since

$$\overline{L}_i = \frac{L_i}{9 \cdot 10^{11}} ,$$

to calculate w_1 one can simply substitute the value $z_i^2/\overline{L}_i$ instead of ξ_i. In this way, w_1 was calculated so that the value of $0.278 \cdot w_1$ could then be entered into the sixth column of Table 5.6. The electrophoretic term was held responsible for the differences between $\alpha/\overline{\Lambda}_{\mathrm{m}}^0$ and $0.278 \cdot w_1$ and backwards the radius $10^8 \cdot b$ calculated. This is how the numbers in the seventh column were obtained. In the row for K_2SO_4, the value for $10^8 \cdot b$ remained blank. Here the value $0.278 \cdot w_1$ would be larger than the value of $\alpha/\overline{\Lambda}_{\mathrm{m}}^0$ derived from the experiments; This would mathematically result in a negative b, which makes no sense. Now one notices that the coefficient β for this salt is negative and shows an abnormally large value. This means that the experimental conductivity curve is strongly curved, in the opposite direction than is usually found. One can therefore consider the value $\alpha/\overline{\Lambda}_{\mathrm{m}}^0 = 0.866$ to be less than certain. In general, negative signs for β occur several times, even in the uni-univalent salts. It should therefore be kept in mind not to overestimate the accuracy of the numbers given for the slope and not to consider the three-digit information as a measure of actual accuracy:

5.2.2. Di-Divalent Salts

Four different di-divalent salts were calculated, again based on observations by Kohlrausch. Not only are the observations less good, the determination of the tangent is also much less certain, since the concentrations at which the observations were made are actually too high for this case of higher valences. It was set

$$\overline{\Lambda}_{\mathrm{m}} = \overline{\Lambda}_{\mathrm{m}}^0 - \alpha \cdot \sqrt{2\gamma} + \beta \cdot (2\gamma) ,$$

and the three coefficients determined from the observations at $\gamma = 0.00005$, $\gamma = 0.0001$, $\gamma = 0.00025$, $\gamma = 0.00050$ and $\gamma = 0.00100$. The results are compiled in Table 5.8. The large values of b are striking, but at present there does not seem to be sufficient reason for us to draw further conclusions from them.

5.3. Non-Aqueous Solvents

The non-aqueous solvents are interesting because one has to expect that the conductivity curve will show the influence of the dielectric constant. As is well known, we owe this particularly to the work of Walden[1] that we have an overview of this area. Walden formulated the overall experience in two sentences. According

[1] [60]; See also the earlier works by the same author given there.

type of salt	$\overline{\Lambda}^0_m$	α	β	$\alpha/\overline{\Lambda}^0_m$	$0,278 \cdot w_1$	$10^8 \cdot b$
$MgSO_4$ ...	229.40	970,7	1067	4.23	2.42	3.8
$ZnSO_4$ ...	230.85	1065,1	1145	4.61	2.40	4.7
$CdSO_4$ ...	231.62	1200,5	1922	5.18	2.39	6.0
$CuSO_4$ ...	230.80	1082,6	684	4.69	2.40	4.9

Table 5.8.: Calculated values of $\overline{\Lambda}^0_m$, α and β of four different types of di-divalent salts

to the first, the product $\overline{\Lambda}^0_m \cdot \eta = K_1$ is constant, i.e.

$$\overline{\Lambda}^0_m \cdot \eta = K_1 \,,$$

namely the larger the ions are and the less the solvent tends to associate[2] the more exact this law is supposed to be. This rule is understandable if the frictional force experienced by the ions can be calculated according to the equations of hydrodynamics in the sense of Stokes and it is clear that this fits more the larger the ions are. On the other hand, since the tendency to associate is obviously linked to the presence of permanent electrical moments of the solvent molecules and as these cause a disturbance in the Stokes flow in the sense of Born, this influence is also to be expected.

The second Walden rule is as follows. If one considers solutions of a salt of the same concentration in different solvents, the difference $\overline{\Lambda}^0_m - \overline{\Lambda}_m$ is antiproportional to the product of the dielectric constant ε and the friction constant η (dynamic viscosity) of the solvent

$$\overline{\Lambda}^0_m - \overline{\Lambda}_m = \frac{K_2}{\varepsilon \cdot \eta} \,.$$

Combining the two rules results in the conductivity coefficient f_λ gives

$$1 - f_\lambda = \frac{\overline{\Lambda}^0_m - \overline{\Lambda}_m}{\overline{\Lambda}^0_m} = \frac{K_2}{K_1} \cdot \frac{1}{\varepsilon} \,.$$

According to the above theory (at a given concentration) the dependence on the dielectric constant is somewhat different. According to Equation 4.9,[3] the following

[2] Water is known to deviate the most from this rule.

[3] The factors of $\varepsilon^{-\frac{3}{2}}$ and $\varepsilon^{-\frac{1}{2}}$ are constant as long as the ratio of mobilities in the different solvents remains the same.

type of solvent	chem. formula	ε	S_1	S_2	$S_1 + S_2$
Nitromethane ..	CH_3NO_2	38.8	0.81	1.33	2.14
Acetonitrile	CH_3CN	36	0.91	1.38	2.29
Nitrobenzene ..	$C_6H_5NO_2$	35.5	0.93	1.39	2.32
Methyl alcohol .	CH_3OH	35.4	0.94	1.57	2.51
Propionitrile ...	C_2H_5CN	27.5	1.37	1.62	2.99
Benzonitrile ...	C_6H_5CN	26	1.48	1.64	3.12
Ethyl alcohol ..	C_2H_5OH	25.4	1.54	1.74	3.28
Epichlorohydrin	C_3H_5ClO	22.6	1.83	1.79	3.62
Acetone	$(CH_3)_2CO$	21.2	2.01	1.79	7.80
Acetophenone .	$C_6H_5COCH_3$	18	2.58	1.95	4.53
Benzaldehyde ..	C_6H_5COH	17	2.82	2.01	4.83

Table 5.9.: Dielectric constant ε of eleven different solvents and summands S_1 and S_2 calculated using ε according to Equation 5.6

holds good:

$$1 - f_\lambda = \frac{\text{const.}}{\varepsilon^{\frac{3}{2}}} + \frac{\text{const.}}{\varepsilon^{\frac{1}{2}}},$$

where the first term stems from the ionic effect and the second term from electrophoresis. Qualitatively, the theory makes the same statement as WALDEN's rule: as the dielectric constant increases, $1 - f_\lambda$ should decrease. In order to see whether the theoretical law also does justice to the observations in the numerical coefficients, we carried out some calculations, which are compiled in the following tables[4]. In Table 5.9 the first column contains the name of the solvent, its chemical formula in the second column and the dielectric constant in the third.

According to Equation 4.9, the theoretical formula is, if instead of n the concen-

[4]Those measurements were selected for which the concentrations were assumed to be sufficiently small.

tration γ is introduced into $\mathrm{mol\,L^{-1}}$,

$$1 - f_\lambda = \left[\frac{e_0^2}{6\varepsilon k_\mathrm{B} T} \cdot \sqrt{\frac{4\pi e_0^2}{\varepsilon k_\mathrm{B} T} \cdot \frac{N_A}{1000}} \cdot w_1 \right. \tag{5.6}$$

$$\left. + b \cdot \sqrt{\frac{4\pi e_0^2}{\varepsilon k_\mathrm{B} T} \cdot \frac{N_A}{1000}} \cdot w_2 \right] \cdot \sqrt{\nu\gamma}\,, \tag{5.7}$$

where N_A denotes the AVOGADRO constant. The salts we will calculate with are all uni-univalent, so $\nu = 2$. We also want to consider the mobilities of the ions to be equal in the valence factor w_1; then $w_1 = 1$. Finally, a mean value shall always be used for b; we choose $b = 4 \times 10^{-8}\,\mathrm{cm}$. Then the two summands in the brackets can be determined numerically. We call the first S_1, the second S_2, their values are entered in Table 5.9 in columns four and five, the sum $S_1 + S_2$ is contained in column six.

The observations were now plotted as a function of $\sqrt{2\gamma}$ and the initial tangent of the curve was drawn graphically for each salt in each solvent. So $\overline{\Lambda}_\mathrm{m}^0$ and α are determined in the representation

$$\overline{\Lambda}_\mathrm{m} = \overline{\Lambda}_\mathrm{m}^0 - \alpha \cdot \sqrt{2\gamma}$$

and $\alpha/\overline{\Lambda}_\mathrm{m}^0$ can be taken from the course of the tangent. In Table 5.10 the name of the solvent is entered in column one and the factor $S_1 + S_2$ taken from Table 5.9 is entered in column two. The following columns contain the values of $\alpha/\overline{\Lambda}_\mathrm{m}^0$ obtained graphically in the manner just sketched, which according to the theory, are to be compared with the values of $S_1 + S_2$.

The observations are not such that one could draw conclusions with great accuracy about the course of the tangent and also show larger differences between different researchers. For example, PHILIPP and COURTMAN find a curve for tetraethylammonium iodide in nitromethane from which $\alpha/\overline{\Lambda}_\mathrm{m}^0 = 1.4$ would follow, while the value given in the table 2.2 follows from the observations of WALDEN. The relationships are illustrated by Figure 5.2, in which observations of KI in methyl alcohol are plotted as a function of $\sqrt{2\gamma}$. The black points are measured by KREIDER and JONES, [47, 46], the green points by PHILIPP and COURTMANN, [55], the ocher ones Points from JONES, BRINGHAM and MC MASTER, [32], the blue points from FISCHLER, [14]. Given these circumstances, we have been content with the above rough calculation. It still seems possible to conclude that the theory is essentially consistent with the observations.

type of solvent	$S_1 + S_2$	$\alpha/\overline{\Lambda}^0_m$			
		KI	NaI	$N(C_2H_5)_4I$	$N(C_3H_7)_4I$
Nitromethane ..	2,14	2.1	–	2.2	–
Acetonitrile	2,29	2.4	2.3	1.9	2.2
Nitrobenzene ..	2,32	–	–	1.9	–
Methyl alcohol .	2,51	2.5	–	2.3	–
Propionitrile ...	2,99	–	–	3.5	–
Benzonitrile ...	3,12	–	3.3	3.7	3.2
Ethyl alcohol ..	3,28	2.5	–	3.2	–
Epichlorohydrin	3,62	–	–	3.2	3.2
Acetone	3,80	3.5	4.2	–	–
Acetophenone .	4,53	–	4.7	–	–
Benzaldehyde ..	4,83	–	–	5.3	–

Table 5.10.: Calculated values of S_1 and S_2 of eleven solvents in which are dissolved four different salts with the appropriate value of $\alpha/\overline{\Lambda}^0_m$

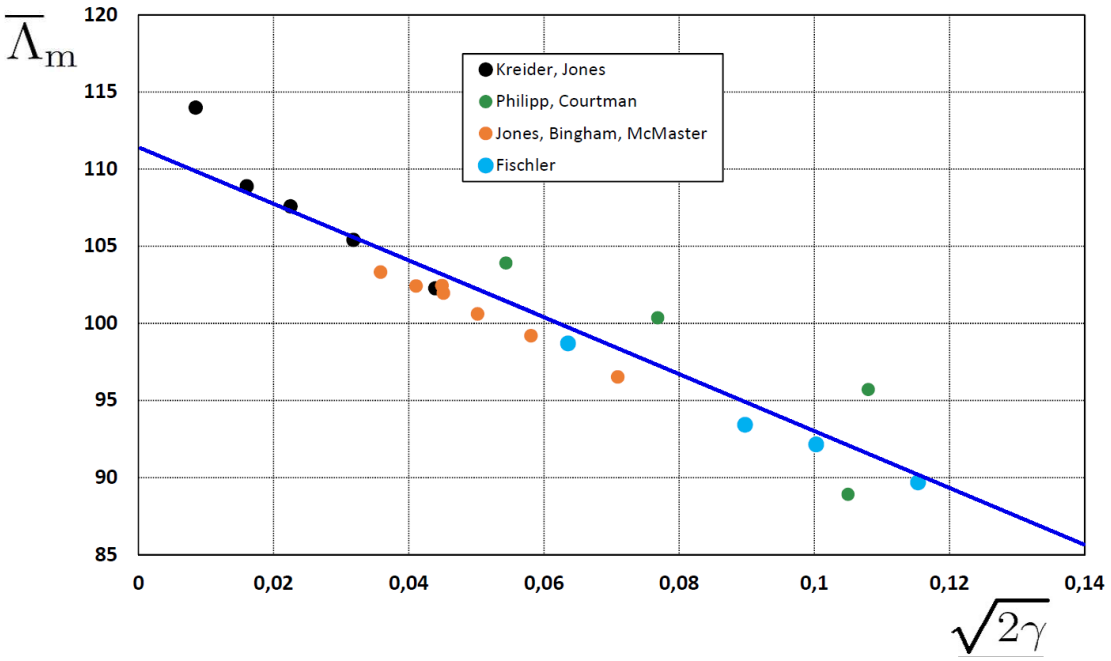

Figure 5.2.: Plot of the molar conductivity of KI in methyl alcohol in dependence of concentration

5.4. Temperature Dependence of the Coefficient of Conductivity

According to Equation 4.9, the conductivity coefficient f_λ contains the temperature only in the relation εT, provided that the mobilities are considered to be independent of the temperature. In order to check to what extent the theory is able to represent the temperature dependence, we were able to use a few observations at 100 °C, which are from Noyes and Coolidge, [53] and Noyes, Melcher, Cooper and Eastman, [54], and are also listed in Kohlrausch and Holborn (p. 210). The observations were plotted and the tangent determined graphically; the designations used here are the same as in section 5.1 and section 5.2. Table 5.11 contains the chemical formulæ of the salts examined in the first column (two uni-univalent, two uni-divalent, one di-divalent). The second column contains the numbers found graphically for $\alpha/\overline{\Lambda}^0_m$. The third column contains values for $\alpha/\overline{\Lambda}^0_m$, which result from the following calculation: The values of b were taken from the numbers given in the previous paragraphs, which are valid at 18 °C. These radii were then considered to be valid also for 100 °C and then the factor of $\sqrt{\nu\gamma}$ in the expression for $1 - f_\lambda$ was calculated using a dielectric constant for 100 °C. The latter was obtained from Drude's formula, [12],

$$\varepsilon = 88.23 - 0.4044 \cdot t + 0.001035 \cdot t^2 \,,$$

type of salt	$\left(\alpha/\overline{\Lambda}^0_{\mathrm{m}}\right)_{\mathrm{obs.}}$	$\left(\alpha/\overline{\Lambda}^0_{\mathrm{m}}\right)_{\mathrm{calc.}}$
NaCl	0.554	0.550
$AgNO_3$ ...	0.573	0.608
$Ba(NO_3)_2$	1.17	1.27
K_2SO_4 ...	1.30	1.12
$MgSO_4$ ...	4.40	4.64

Table 5.11.: Observed and calculated values of $\alpha/\overline{\Lambda}^0_{\mathrm{m}}$ at 100 °C for five different salts. Observed values derived from graphical interpretation

although this formula is actually only valid up to 76 °C. One finds $\varepsilon = 58.14$. For K_2SO_4 the calculation is a very rough one. In fact, in section 5.2 the case of K_2SO_4 was precisely the one in which the conductivity curve showed a strong and unlikely negative curvature, resulting in a negative value of b. Here, since there is no value of b present, we have set $b = 0$, which must obviously lead to a value of the calculated slope that is too small. As far as it is possible to judge, the theoretical temperature dependence appears to correspond to the observations.

Zurich, July 1923

(Received July 19, 1923)

Part III.

Appendix

In the following, I will attempt to explain how the value 3.06×10^{-8} cm is obtained and show the related, simple but rather confusing calculation. The "problem" here is that this article was written from the perspective of the c.g.s. (centimeter-gram-second) system (correctly referred to as GAUSSian cgs units). To make matters more difficult, the dielectric constant, i.e., the relative (material-dependent) permittivity, sometimes has a unit and sometimes does not. The symbol is always the same, namely ε, but often refers to different "versions" of permittivity. The terms commonly used today, permittivity of vacuum ε_0, relative permittivity ε_r, and (absolute) permittivity ε, are jumbled together here, so to speak. This may be due to the fact that unlike in the SI system of units, the GAUSS system does not include vacuum permittivity, i.e., the natural constant ε_0, originally referred to as the influence constant. It is assigned the value 1. But the units are preserved.

The value 3.06×10^{-8} cm is calculated as follows:

In the equation

$$\frac{1}{\varkappa} = \sqrt{\frac{\varepsilon k_\mathrm{B} T}{8\pi n e_0^2}}$$

we have the following constants, whereby the older values of the natural constants are used first in the following:

Formula symbol, Name	Value, Unit
ε, relative permittivity	88,23 (Water)
k_B, BOLTZMANN constant	$1.346 \times 10^{-16}\,\mathrm{erg\,Grad^{-1}}$
T, Temperature	273 K
$n = N_A \cdot \gamma$, number of ions in moles per litre, $\mathrm{mol\,L^{-1}}$; equals LOSCHMIDT number (for one mole) · concentration in $\mathrm{mol\,L^{-1}}$	$6.06 \times 10^{23} \cdot 1\,\mathrm{mol\,L^{-1}}$ or $6.06 \times 10^{23} \cdot \frac{1\,\mathrm{mol}}{1000\,\mathrm{cm^3}}$
e_0, charge of ion, equals elementary charge in c.g.s unit, which is e_0 (c.g.s) $= e_0 \cdot 3 \times 10^9$	4.77×10^{-10} e.s.u.

Putting all these values in the formula above gives

$$\sqrt{\frac{88.23 \cdot 1.346 \times 10^{-16} \cdot 273}{8 \cdot 3.1416 \cdot 6.06 \times 10^{23} \cdot (4.77 \times 10^{-10})^2 \cdot \frac{1}{1000}}}$$

which finally yields, evaluated with Excel, 3.0587×10^{-8} cm, i.e., approximately 3.06×10^{-8} cm.

The same procedure can also be carried out with current values of the natural constants in SI units and the value of ε for water. As indicated above, it is important

to note that we are working in the original GAUSSian c.g.s. system.
However, when we switch to the SI unit system, the permittivity of vacuum ε_0 is set no longer equal to 1. But, in the equation for $\frac{1}{\varkappa}$, only the material-dependent permittivity, i.e. the relative permittivity, appears.
By rearranging the equation slightly and taking into account the conversion from the c.g.s system to the SI system of units using defined constants, we can introduce the permittivity of vacuum ε_0. To do this, we use the approach, for example according to Becker-Sauter, [58], that the permittivity of vacuum is given by:

$$\varepsilon_0 = 8.854\,187\,818\,8 \times 10^{-12}\,\frac{\mathrm{A\,s}}{\mathrm{V\,m}} \cong \frac{1}{4 \cdot \pi \cdot 9 \times 10^9}\,\frac{\mathrm{A\,s}}{\mathrm{V\,m}}$$

and use the fact that in the denominator of the fraction, the value mentioned is already given by the factors $8\pi = 2 \cdot 4\pi$ and $3 \cdot 3 \cdot 1 \times 10^9 \cdot 1 \times 10^9$. The latter term comes from the conversion to coulombs of e_0^2 based on the GAUSSian c.g.s. system:

Größe		SI-Einheit	Konversion in CGS-Einheiten			in Basiseinheiten	
			esE	Gauß	emE	SI	Gauß
elektr. Ladung	Q	Coulomb (C)= A·s	$3 \cdot 10^9$ statC (Fr)		10^{-1} abC	A·s	$g^{1/2} \cdot cm^{3/2} \cdot$

Now we combine the relevant terms and write ε_0 for them.
Therefore, the denominator of the fraction contains the remaining factor 1×10^9.
The value 1000 in the previous equation is known to correspond to $1\,\mathrm{L} = 1000\,\mathrm{cm}^3$.
This value must now be expressed in m^3, which corresponds to $1 \times 10^6\,\mathrm{cm}^3$.

So once again we have:

$$\sqrt{\frac{\varepsilon_0 \cdot 80.2 \cdot 1.380\,649 \times 10^{-23} \cdot 273.15}{2 \cdot 6.022\,140\,76 \times 10^{23} \cdot (1.602\,176\,634 \times 10^{-19})^2 \cdot \frac{1}{1 \times 10^6} \cdot 1 \times 10^9}}\,,$$

which corresponds to the formula given in Wikipedia, since the resultant in the denominator is 2000. The value obtained in this way is $2.943 \times 10^{-10}\,\mathrm{m}$ or 0.294 nm for 0 °C.
The Δ of both values is approximately 1.040, which circumstance is not relevant for practical purposes.

For $T = 293\,\mathrm{K}$ there results $3.048 \times 10^{-10}\,\mathrm{m}$, which equals the value given in the English Wikipedia

$$\kappa^{-1}(\mathrm{nm}) = \frac{0.304}{\sqrt{I(\mathrm{M})}}\,.$$

Part IV.

Literature

Bibliography

[1] L. H. Adams. The Measurement of the Freezing-Point Depression of Dilute Solutions. *Journal of the American Chemical Society*, 37(3):481–496, 1915. (KCl).

[2] J. Barnes. On the depression of the freezing-point by mixtures of electrolytes. In J. Davidson and J. E. Gilpin, editors, *Proceedings and Transactions of the Nova Scotian Institute of Science*, volume 10, pages 139–161. Printed for the Institute by McAlpine Publishing Co., Ltd., 1900.

[3] G. P. Baxter and C. C. Wallace. Changes in Volume upon Solution in Water of Halogen Salts of Alkali Metals. II. *Journal of the American Chemical Society*, 38(1):70–105, 1916.

[4] T. G. Bedford. The depression of freezing point in very dilute aqueous solutions. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 83(565):454–461, 1910. ($CuSO_4$).

[5] W. Biltz. Zur Kenntnis der Lösungen anorganischer Salze in Wasser. *Zeitschrift für physikalische Chemie*, 40:185–221, 1902.

[6] N. Bjerrum. A new form for the electrolytic dissociation theory. Seventh International Congress of Applied Chemistry, May 27$^{\text{th}}$ to June 2$^{\text{nd}}$, Section X: Electro-chemistry. Physical chemistry, pages 55–60, London, 1909. Partridge & Cooper, Ltd.

[7] N. Bjerrum. De stærke Elektrolytters Dissociation. *Forhandlinger ved de Skandinaviske Naturforskeres Møde*, pages 226–242, 10.-15. Juli 1916 1918. 16. Møte i Kristiania, see also english translation [9].

[8] N. Bjerrum. Der Aktivitätskoeffizient der Ionen. *Zeitschrift für anorganische und allgemeine Chemie*, 109(1):275–292, 1919.

[9] N. Bjerrum. The Dissociation of Strong Electrolytes. In H. M. Leicester, editor, *Source Book in Chemistry 1900–1950*, volume 10 of *Source Books in the History of the Science*, pages 181–188. Harvard University Press, 1968.

[10] M. Born. Über die Beweglichkeit der elektrolytischen Ionen. *Zeitschrift für Physik*, 1(3):221–249, 1920.

[11] B. A. M. Cavanagh. Molecular thermodynamics. I. *Philosophical Magazine*, 43(255):606–636, 1922.

[12] P. Drude. Der electrische Brechungsexponent von Wasser und wässerigen Lösungen. *Annalen der Physik*, 59:17–62, 1896. see pp. 50, 61.

[13] L. Ebert. *Forschungen über die Anomalien starker Elektrolyte*, volume 18 of *Jahrbuch der Radioaktivität und Elektronik*, page 134. Leipzig, S. Hirzel, 1921.

[14] J. Fischler. Über molekulare Leitfähigkeit und innere Reibung in Gemischen von Methylalkohol bezw. Aceton mit Benzol und Nitrobenzol. *Zeitschrift für Elektrochemie*, 19(3):126–132, 1913.

[15] F. Flügel. Über Gefrierpunktsbestimmungen stark verdünnter wässeriger Lösungen. *Zeitschrift für physikalische Chemie*, 79(5):577–591, 1912.

[16] Ch. J. Ghosh. The abnormality of strong electrolytes. Part I. Electrical conductivity of aqueous salt solutions. *Journal of the Chemical Society, Transactions*, 113:449–458, 1918.

[17] Ch. J. Ghosh. The abnormality of strong electrolytes. Part II. The electrical conductivity of non-aqueous solutions. *Journal of the Chemical Society, Transactions*, 113:627–638, 1918.

[18] Ch. J. Ghosh. The abnormality of strong electrolytes. Part III. The osmotic pressure of salt solutions and equilibrium between electrolytes. *Journal of the Chemical Society, Transactions*, 113:707–715, 1918.

[19] Ch. J. Ghosh. The electrical conductivity of acids and bases in aqueous solutions. *Journal of the Chemical Society, Transactions*, 113:790–799, 1918.

[20] Ch. J. Ghosh. Eine allgemeine Theorie der Elektrolytlösungen. *Zeitschrift für physikalische Chemie*, 98(3/4):211–238, 1921.

[21] M Gouy. Sur la constitution de la charge électrique à la surface d'un électrolyte. *Journal de Physique Théorique et Appliquée*, 9(4):457–467, 1910.

[22] R. E. Hall and W. D. Harkins. The Free Energy of Dilution and the Freezing-Point Lowerings in Solutions of some Salts of Various Types of Ionization, and of Salt Mixtures. *Journal of the American Chemical Society*, 38(12):2658–2676, 1916. (K_2SO_4, $La(NO_3)_3$, $MgSO_4$).

[23] C. H. Hamann, A. Hamnett, and W. Vielstich. *Electrochemistry*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2nd edition, 2007.

[24] W. D. Harkins and W. A. Roberts. The Freezing-Point Lowerings in Aqueous Solutions of Salts and Mixtures of Salts and of a Salt with a Nonelectrolyte. *Journal of the American Chemical Society*, 38(12):2676–2679, 1916. (NaCl).

[25] T. C. Hebb. On the determination of the freezing-point depressions of dilute solutions of electrolytes. In J. Davidson and J. E. Gilpin, editors, *Proceedings and Transactions of the Nova Scotian Institute of Science*, volume 10, pages 422–432. Printed for the Institute by McAlpine Publishing Co., Ltd., 1903.

[26] P. Hertz. Über die Abhängigkeit des Leitvermögens binärer normaler Elektrolyte von der Konzentration. *Annalen der Physik*, 37:1–28, 1912.

[27] J. Herweg. Die elektrischen Dipole in flüssigen Dielektricis. *Zeitschrift für Physik*, 3(1):36–47, 1920.

[28] J. Herweg and W. Pötzsch. Die elektrischen Dipole in flüssigen Dielektricis. *Zeitschrift für Physik*, 8:1–12, 1922.

[29] H. Jahn. Über die Erniedrigung des Gefrierpunktes in den verdünnten Auflösungen stark dissociierter Elektrolyte. *Zeitschrift für Physikalische Chemie*, 50:129–168, 1905. (LiCl, CsCl).

[30] H. Jahn. Über die Erniedrigung des Gefrierpunktes in den verdünnten Lösungen stark dissociierter Elektrolyte. II. *Zeitschrift für Physikalische Chemie*, 59:31–40, 1907. (LiCl, CsCl).

[31] H. C.. Jones, J. Barnes, and E. P. Hyde. The lowering of freezing point of aqueous hydrogen dioxide. *American Chemical Journal*, 27:22, 1902.

[32] H. C. Jones, E. C. Bingham, and L. McMaster. Über Leitfähigkeit und innere Reibung von Lösungen gewisser Salze in den Lösungsmittelgemischen: Wasser, Methylalkohol, Äthylalkohol und Aceton. *Zeitschrift für physikalische Chemie*, 57:193–243, 1907.

[33] H. C. Jones and C. G. Carroll. The lowering of the freezing point of aqueous hydrogen dioxide produced by certain salts and acids. *American Chemical Journal*, 28:284, 1902.

[34] F. Kohlrausch. Über das Leitungsvermögen einiger Electrolyte in äusserst verdünnter wässeriger Lösung. *Wiedemanns Annalen*, 26:161–226, 1885.

[35] F. Kohlrausch. Über Ionenbeweglichkeiten im Wasser. *Zeitschrift für Elektrochemie*, 13(25):333–344, 1907.

[36] F. Kohlrausch. Das Leitvermögen wäßriger Lösungen von Elektrolyten mit ein- und zweiwertigen Ionen. In W. Hallwachs, A. Heydweiller, K. Strecker, and O. Wiener, editors, *Gesammelte Abhandlungen von Friedrich Kohlrausch*, volume 2, pages 1223–1267. Verlag von J. A. Barth, Leipzig, 1911. p. 1266.

[37] F. Kohlrausch. Die Äquivalentleitvermögen und die Ionenbeweglichkeiten in unendlicher Verdünnung: Schlußwerte. In W. Hallwachs, A. Heydweiller, K. Strecker, and O. Wiener, editors, *Gesammelte Abhandlungen von Friedrich Kohlrausch*, volume 2, pages 906–911. Verlag von J. A. Barth, Leipzig, 1911. p. 906.

[38] F. Kohlrausch. Ober Ionenbeweglichkeiten im Wasser. In W. Hallwachs, A. Heydweiller, K. Strecker, and O. Wiener, editors, *Gesammelte Abhandlungen von Friedrich Kohlrausch*, volume 2, pages 1119–1145. Verlag von J. A. Barth, Leipzig, 1911. pp. 1134.

[39] F. Kohlrausch. Über das elektrische Leitvermögen von Lösungen der Alkalijodate und eine Formel zur Berechnung von Leitvermögen. In W. Hallwachs, A. Heydweiller, K. Strecker, and O. Wiener, editors, *Gesammelte Abhandlungen von Friedrich Kohlrausch*, volume 2, pages 942–949. Verlag von J. A. Barth, Leipzig, 1911. p. 943.

[40] F. Kohlrausch. Über das Leitungsvermögen einiger Elektrolyte in äußerst verdünnter wäßriger Lösung. In W. Hallwachs, A. Heydweiller, K. Strecker, and O. Wiener, editors, *Gesammelte Abhandlungen von Friedrich Kohlrausch*, volume 2, pages 320–385. Verlag von J. A. Barth, Leipzig, 1911. p. 360.

[41] F. Kohlrausch. Über Ionenbeweglichkeiten im Wasser. In W. Hallwachs, A. Heydweiller, K. Strecker, and O. Wiener, editors, *Gesammelte Abhandlungen von Friedrich Kohlrausch*, volume 2, pages 1119–1145. Verlag von J. A. Barth, Leipzig, 1911. pp. 1127, 1132.

[42] F. Kohlrausch. Über Ionenbeweglichkeiten im Wasser. In W. Hallwachs, A. Heydweiller, K. Strecker, and O. Wiener, editors, *Gesammelte Abhandlungen von Friedrich Kohlrausch*, volume 2, pages 1119–1145. Verlag von J. A. Barth, Leipzig, 1911. pp. 1127.

[43] F. Kohlrausch and L. Holborn. *Das Leitvermögen der Elektrolyte insbesondere der wässrigen Lösungen*. Teubner, Leipzig, 2 edition, 1916. pp. 108 and 112.

[44] F. Kohlrausch and M. E. Maltby. Das elektrische Leitvermögen wässriger Lösungen von Alkali-Chloriden und Nitraten. *Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt*, 3:155–227, 1900.

[45] Ch. A. Kraus and H. C. Parker. The Calibration of Cells for Conductance Measurements. *Journal of the American Chemical Society*, 44(11):2422–2428, 1922.

[46] R. Kreider and H. C. Jones. The Conductivity of Certain Salts in Methyl and Ethyl Alcohol at High Dilutions. *American Chemical Journal*, 46:574–585, 1911.

[47] R. Kreider and H. C. Jones. The Dissociation of Electrolytes in Nonaqueous Solvents as Determined by the Conductivity and Boiling-Point Methods. *American Chemical Journal*, 45:282–324, 1911.

[48] N. Lakshminarayanaiah and P. C. Bianchi. Ion Association of Simple Electrolytes in Water Saturated 1-Butanol. *Biophysical Journal*, 8(8):965–970, 1968.

[49] S. R. Milner. The virial of a mixture of ions. *Philosophical Magazine*, 23(136):551–578, 1912.

[50] S. R. Milner. The virial of a mixture of ions. *Philosophical Magazine*, 23(136):551–578, 1912. p. 575.

[51] S. R. Milner. The effect of interionic forces on the osmotic pressure of electrolytes. *Philosophical Magazine*, 25(149):742–751, 1913.

[52] W. Nernst. Untersuchungen über die spezifische Wärme bei tiefen Temperaturen. II. *Königlich Preußische Akademie der Wissenschaften (Berlin). Sitzungsbericht*, 1:262–282, 1910.

[53] A. A. Noyes and W. D. Coolidge. The Electrical Conductivity of Aqueons Solutions at High Temperatures. First Paper. Description of the Apparatus. Results with Sodium- and Potassium Chlorides up to 306°. *Zeitschrift für physikalische Chemie*, 46:323–378, 1903.

[54] A. A. Noyes, A. C. Melcher, H. C. Cooper, and G. W. Eastman. The Conductivity and Ionization of Salts, Acids, and Bases in Aqueous Solutions at High Temperatures. *Zeitschrift für physikalische Chemie*, 70:335–377, 1910.

[55] J. Ch. Philipp and H. R. Courtman. Behaviour of two salts with a common ion, when dissolved in an organic solvent. *Journal of the Chemical Society, Transactions*, 97:1261–1271, 1910.

[56] T. W. Richards. Die Gefrierpunkte verdünnter Lösungen. *Zeitschrift für physikalische Chemie*, 44:563–570, 1903.

[57] W. H. Rodebusch. The Freezing Points of Concentrated Solutions and the Free Energy of Solution of Salts. *Journal of the American Chemical Society*, 40(8):1204–1213, 1918.

[58] F. Sauter and R. Becker. *Theorie der Elektrizität. Band 1: Einführung in die Maxwellsche Theorie, Elektronentheorie. Relativitätstheorie.* B.G. Teubner Stuttgart, 21 edition, 1973. page 10.

[59] W. Sutherland. Ionization in solutions and two new types of viscosity. *Philosophical Magazine*, 14(79):1–35, 1907.

[60] P. Walden. Über die Grenzwerte Λ_∞ der molekularen Leitfähigkeit in nichtwäßrigen und wäßrigen Lösungen. *Zeitschrift für anorganische und allgemeine Chemie*, 115(1):49–86, 1920.

[61] E. W. Washburn and D. A. MacInnes. The Laws Of "Concentrated" Solutions. III. The Ionization and Hydration Relations of Electrolytes in Aqueous Solution at Zero Degrees: A. Cesium Nitrate, Potassium Chloride and Lithium Chloride. *Journal of the American Chemical Society*, 33(11):1686–1713, 1911. (LiCl, $CsNO_3$).

[62] H. J. Weiland. The Equivalent Conductance of Electrolytes in Dilute Aqueous Solution. III. A Study of Dilute Solutions of Potassium Chloride. *Journal of the American Chemical Society*, 40(1):131–150, 1918.

[63] S. W. Young and W. H. Sloan. A Modification of the Freezing-Point Method. *Journal of the American Chemical Society*, 26(8):913–922, 1904.